11-13-2015

Controlling Surface Chemistry of Liquid Metals to Enhance their Fluidic Properties

Nahid Ilyas

Controlling Surface Chemistry of Liquid Metals to Enhance their Fluidic Properties

November 13, 2015

Nahid Ilyas

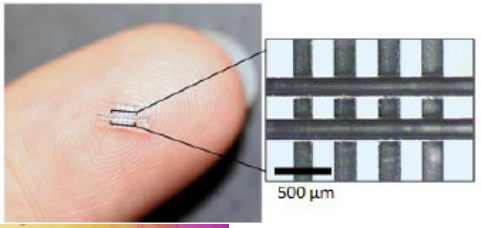
Air Force Research Laboratory
UES, Inc.

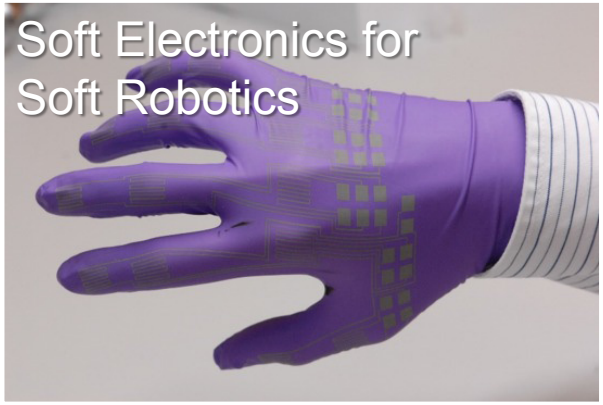
Integrity ★ Service ★ Excellence

Excellence in Science & Technology

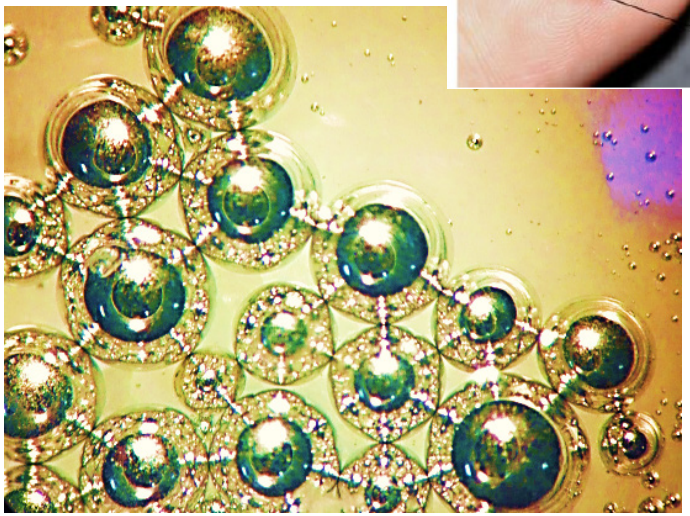
Room Temperature Liquid Metals

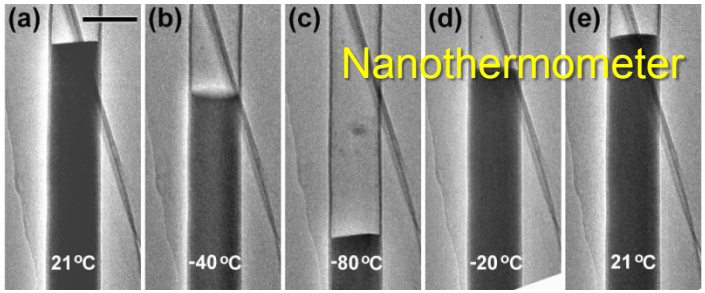
Liquid Conductors





Proc. of SPIE
Vol. 9467
946707-1



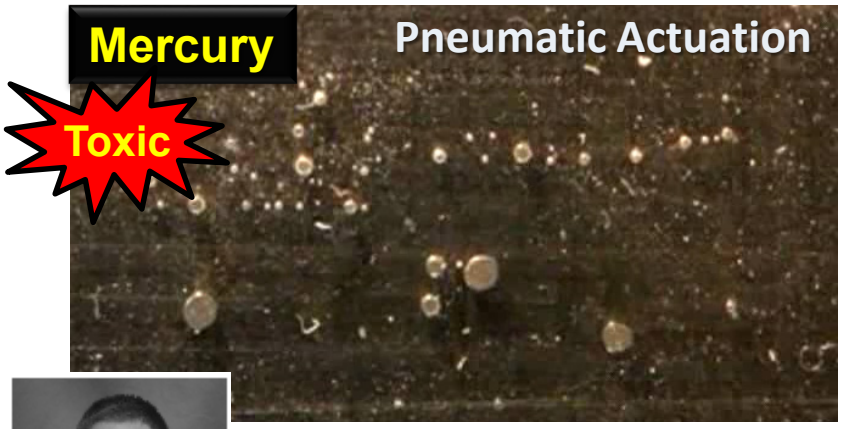


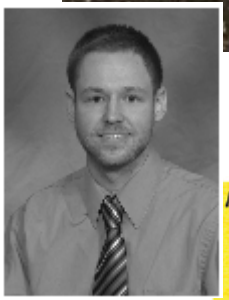
PRL, *93*,
2004, 95504

Ga in Carbon Nanotubes

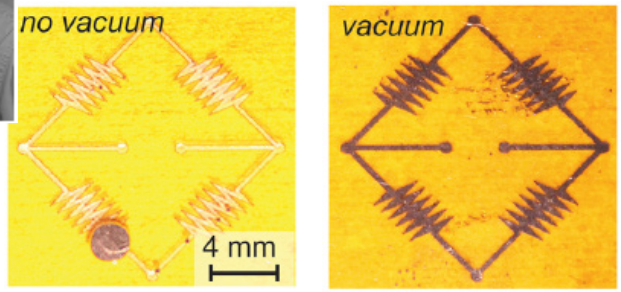
Reconfigurable Circuits
Possible Only with Liquid Conductors

Reconfigurability achieved by





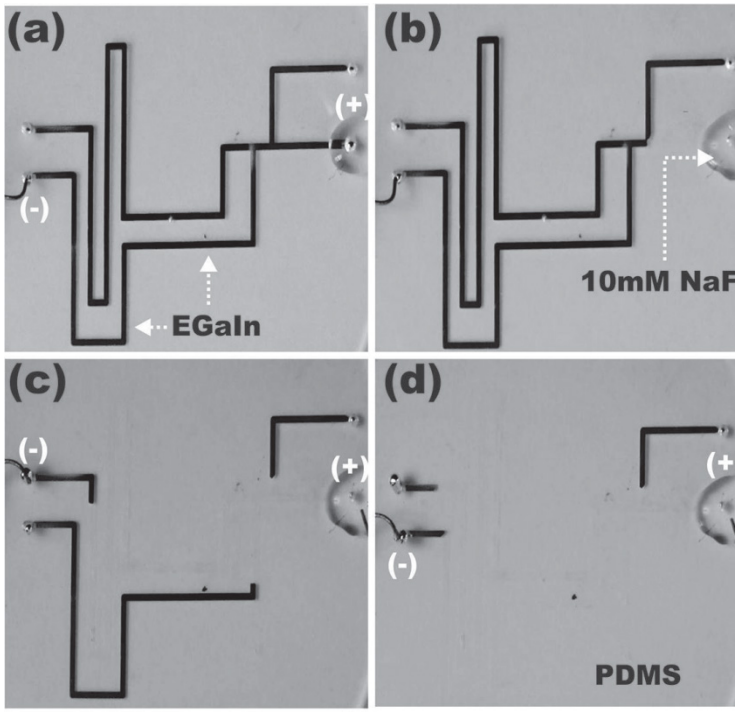
Brad Cumby, AFRL



B. Cumby *et al*, *Appl. Phys. Lett.* **101** (2012) 174102

Nontoxic Liquid Metal (Gallium alloys)

Electrochemistry



M. R. Khan *et al.*, *Adv. Funct. Mater. (2014) available online*

Non-Toxic Room Temperature Liquid Metals
Gallium Liquid Metal Alloys (GaLMA)

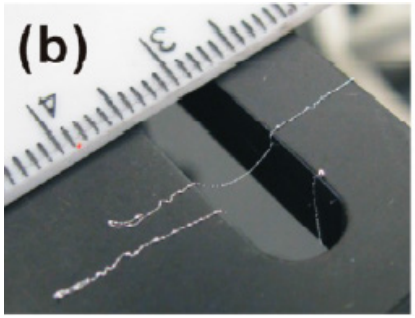
The Oxide Skin is Solid

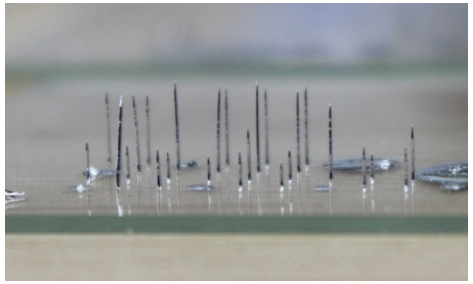
Lowers the surface tension of liquid metal and allows it to conform into various 3D structure

3D Printing of Liquids ! ! !

Non-Toxic Alternative to Hg

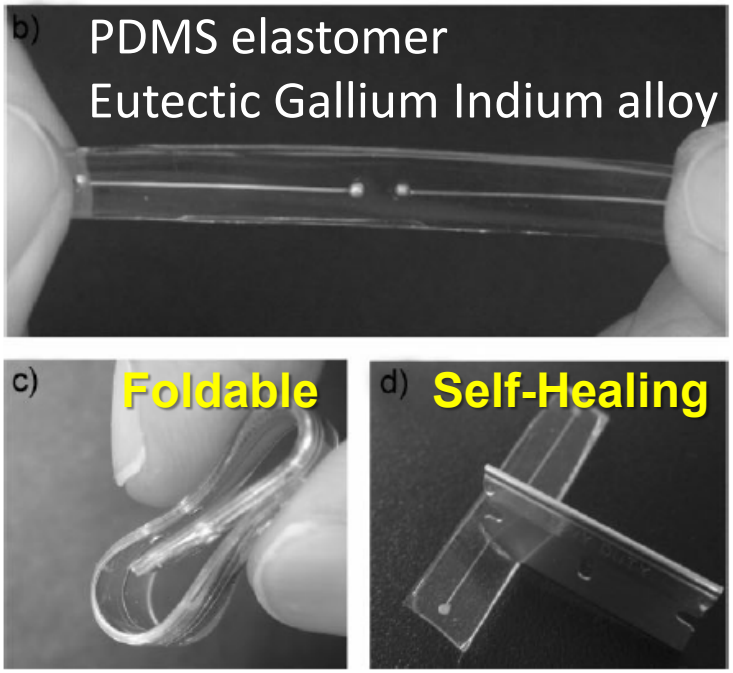
Printed by **Alex Cook**, RXAS (Flex Group)





C. Ladd et al. *Adv. Mater.* **2013** *25* 5081-5085

Reversibly Deformable Dipole Antenna Gallium Liquid Metal Alloys (GaLMA)

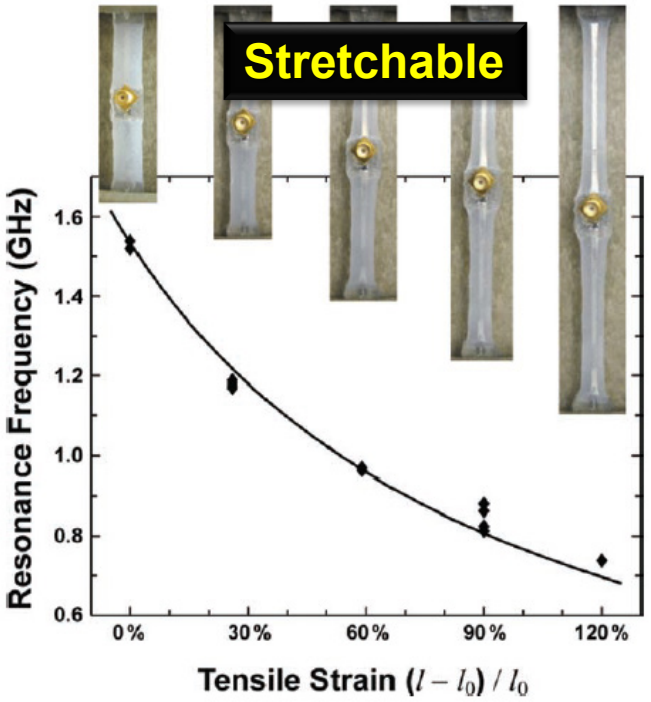


No hysteresis in the spectral properties of the antenna

Antenna **self-heals** in response to sharp cuts

J.-H. So et al., *Adv. Funct. Mater.* **19** (2009) 3632-3637

EGaIn embedded in microfluidic channels composed of PDMS and Ecoflex.



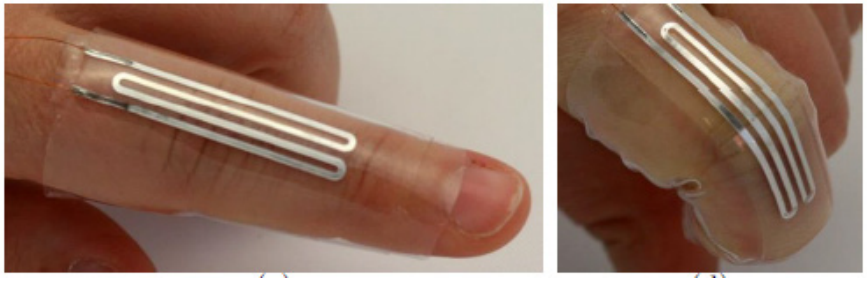
M. Kubo *et al*, *Adv. Mater.* **22** (2010) 2749-2752

GaLMA
Non-Toxic Material for Flexible Electronics

Melting Points

- Ga : 29.77 °C (85.59 °F)
- **EGaIn**: 15.7 °C (60.6 °F)
- GaInSn : -19 °C (-2 °F)

Soft Electronics for Soft Robotics

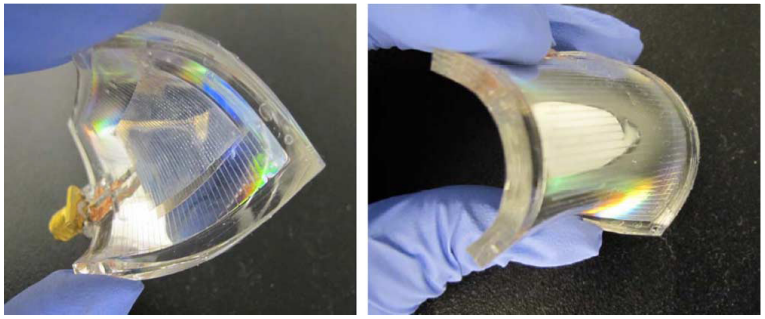


Proc. of SPIE Vol. 9467 946707-1

Gallium Alloy Properties
Viscosity ≈ Water
Vapor pressure ≈ 0

Liquid Metal encapsulated in Elastomer

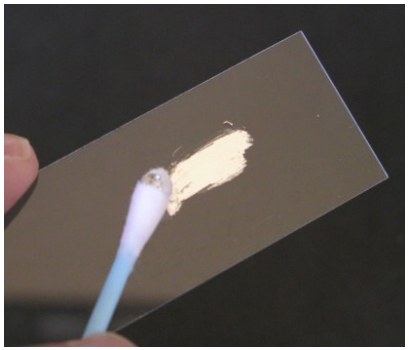
Microstrip Patch Antenna

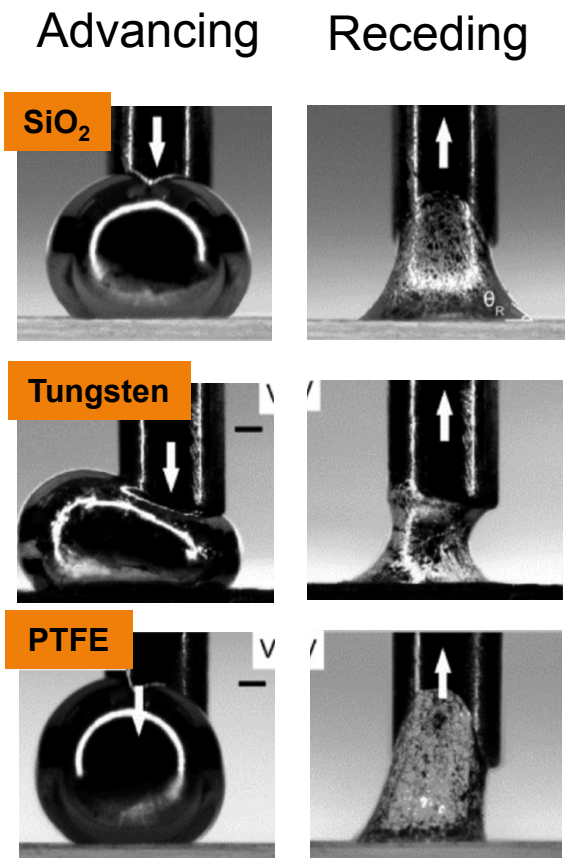


IEEE TRANSACTIONS ON ANTENNAS AND PROPAGATION, *60(5)*, **2012**, 2151-2156

CHALLENGES
Reconfigurability in Microfluidic Systems

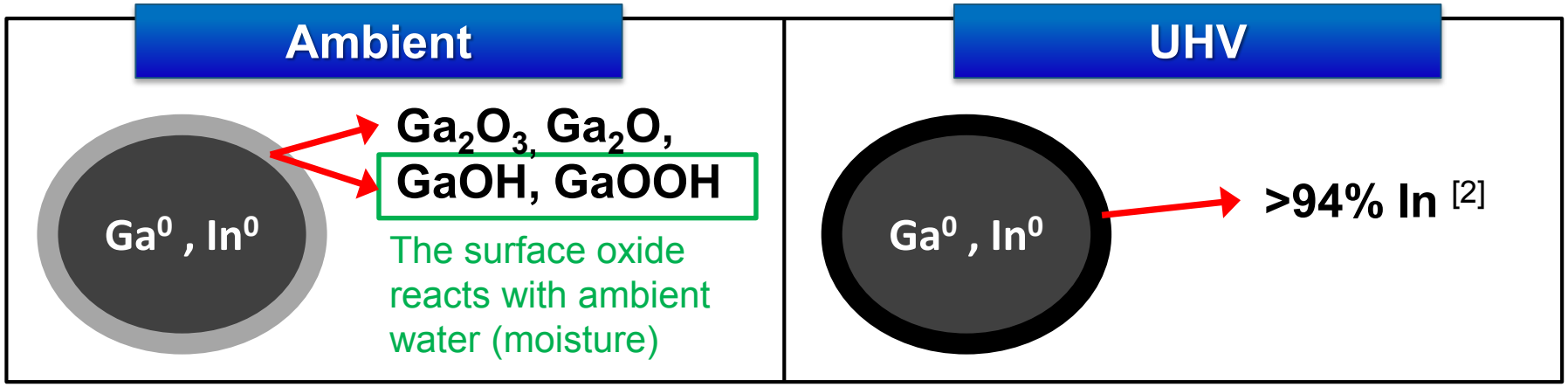
Surface Oxide Permanently Adheres to Most Surfaces





K. Doudrick *et al.*, *Langmuir* **30** (2014) 6867−6877

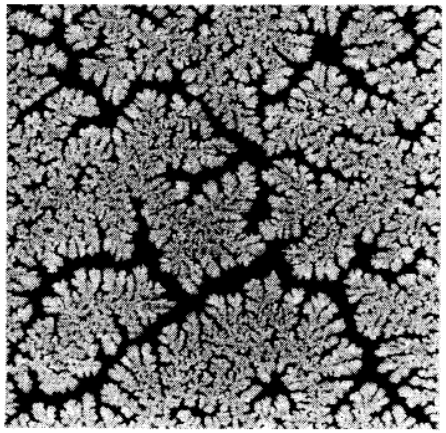
Liquid Metal with a Thin Solid Skin



Thin solid layer on the surface:

- ✓ Native Oxide – instantaneously forms
- ✓ As thick as 20 nm: XRD[1] and XPS
- ✓ Amorphous: XRD[1]
- ✓ Stabilizes – allows 3D printing

After 40 min of exposure to O_2 at partial pressure of 5.0×10^{-7} Torr



SIMS Imaging in UHV [3]

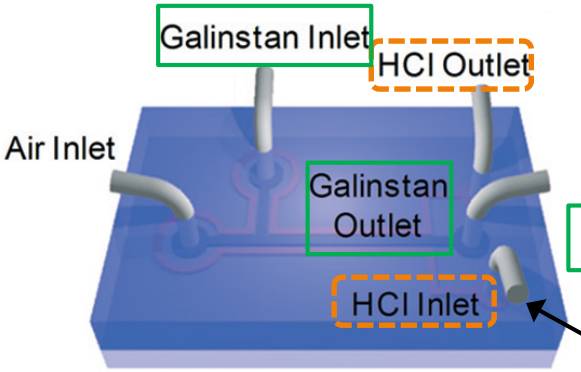
[1] Phys. Rev. B, *55*, **1997**, 786-790.
[2] Surf. Sci., *24*, **1983**, 407-422.
[3] Phys. Rev. B., *46*, **1992**, 11346-11357.

Methods Proposed in Literature to Alleviate these Problems in Device Fabrication & Operation

Coplanar microfluidic channels

Caustic Solutions

Filling the channels with HCl solution NOT PRACTICAL ! ! !



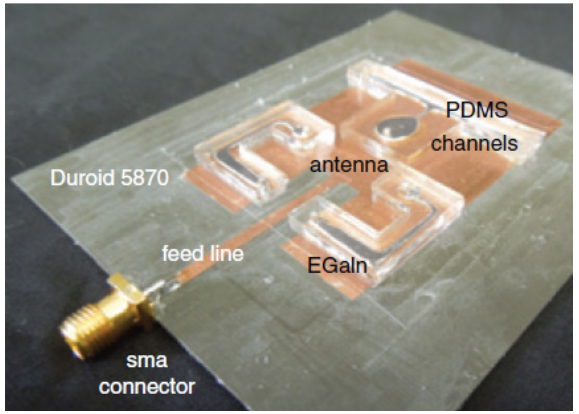
Use of HCl solutions of high concentration NOT PRACTICAL ! ! !

Galinstan: GaInSn

12 M HCl

Li, G., et al. *Lab Chip*, **14** (2014) 200

Frequency reconfigurable patch antenna



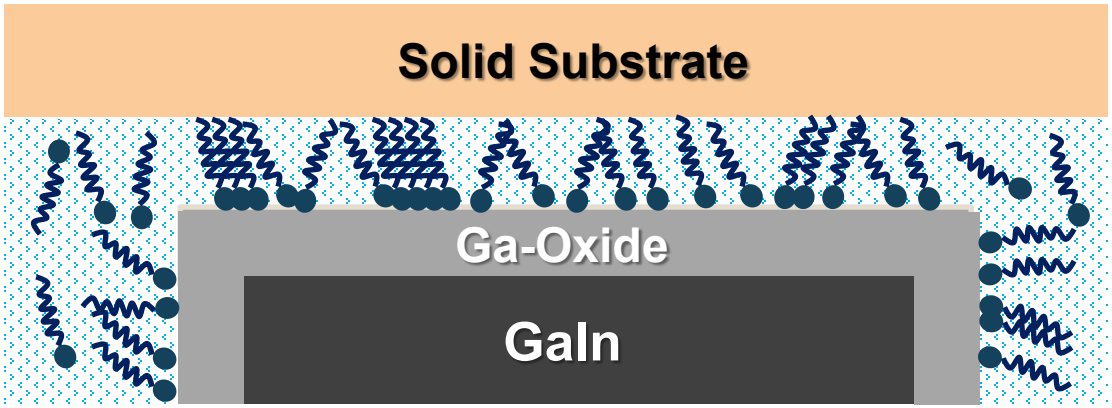
M. Kelley, et al. *Elect. Lett.*, **49** (2013) 1370-1371

GaLMA exposed to HCl vapor

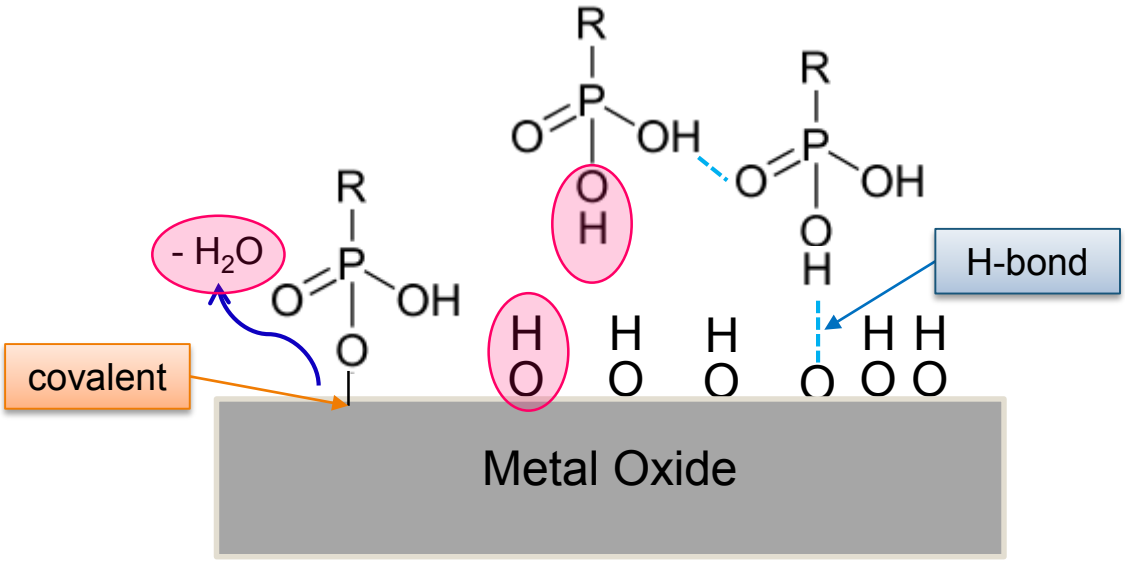
M. Dickey, NC State U.

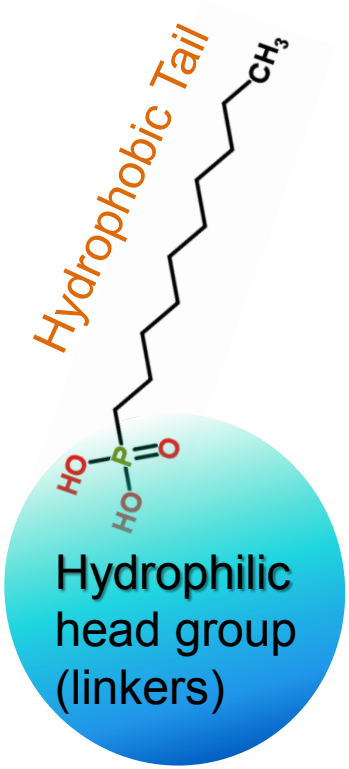
Need an Alternative Method to Replace HCl

An Interface Modification Layer To Protect the Surface Oxide of GaLMA

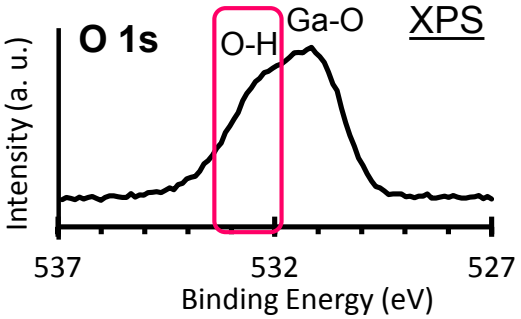


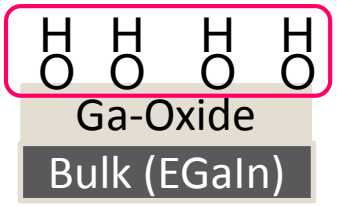
Alkyl Phosphonic Acids

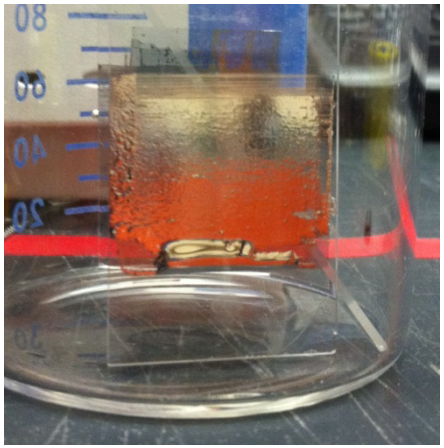




Contact Angle of H_2O - Modification of Surface Wettability of EGaIn (Eutectic GaIn)

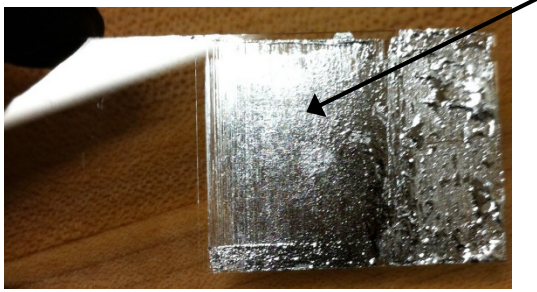


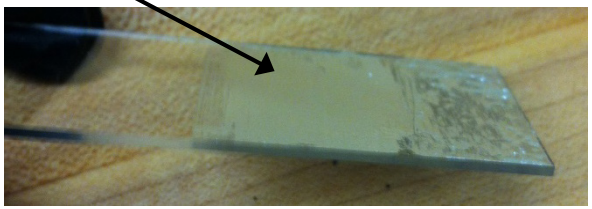




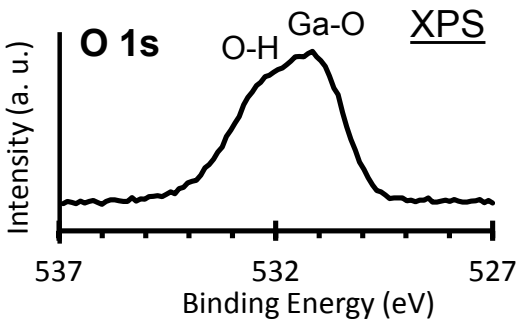
Doctor-bladed: tilted to remove excess EGaIn.

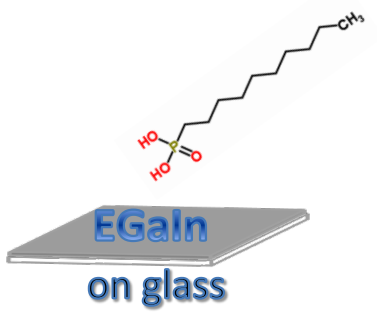
Contact angle of H_2O measured on smooth areas of the surface.

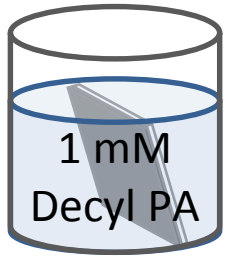




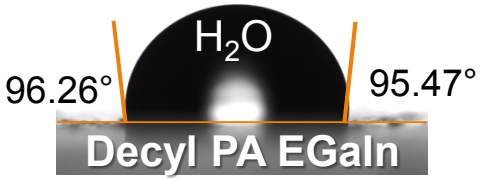
Decyl Phosphonic Acids Make the EGaIn Surface Hydrophobic

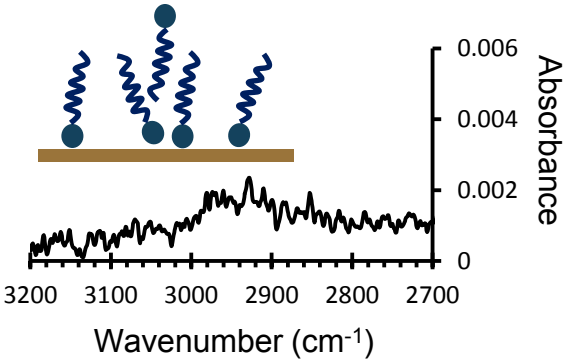






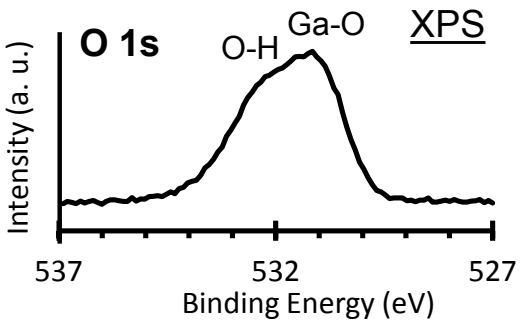
1 mM, 10 sec

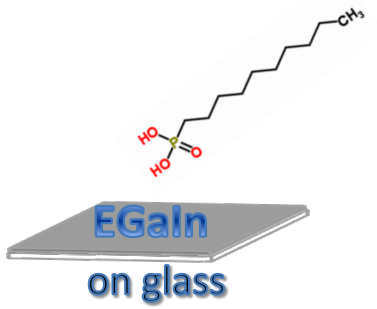


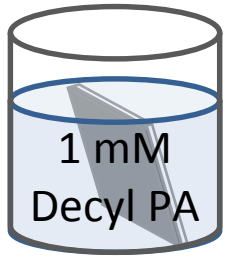


ATR-FTIR: all background subtracted

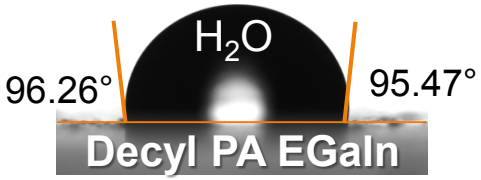
Decyl Phosphonic Acids Make the EGaIn Surface Hydrophobic

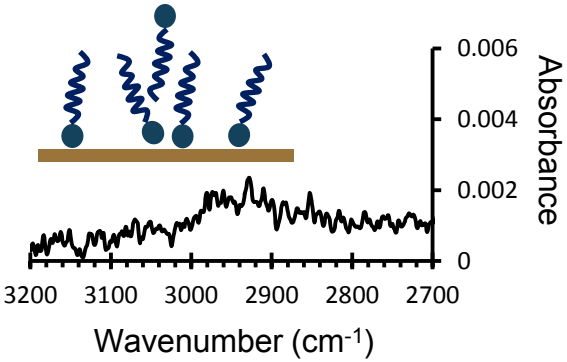




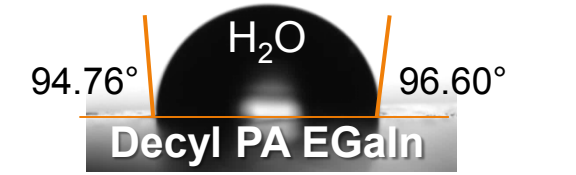


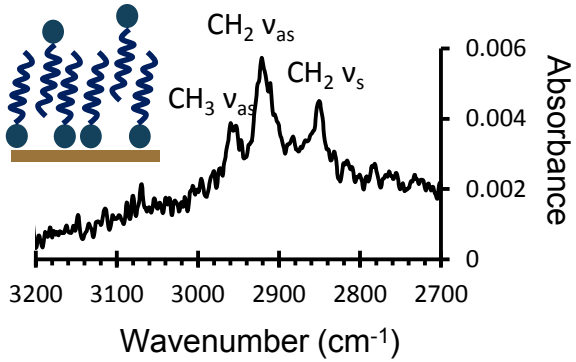
1 mM, 10 sec





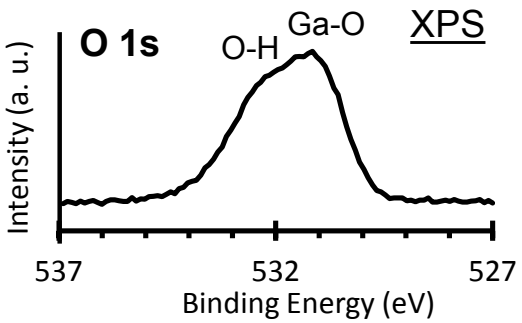
1 mM, 5 min

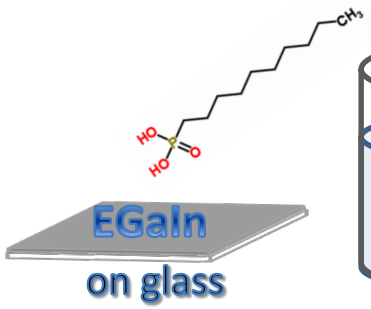


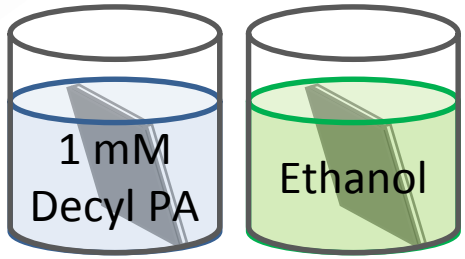


ATR-FTIR: all background subtracted

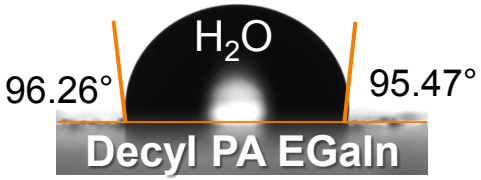
Decyl Phosphonic Acids Make the EGaIn Surface Hydrophobic

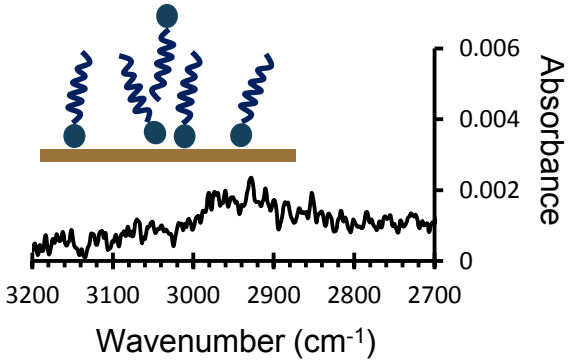




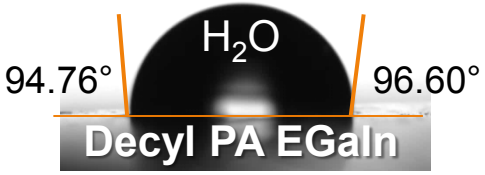


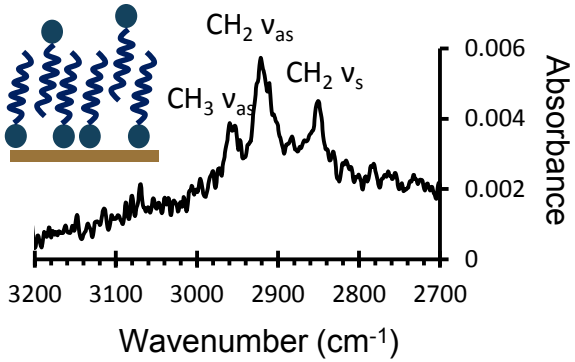
1 mM, 10 sec



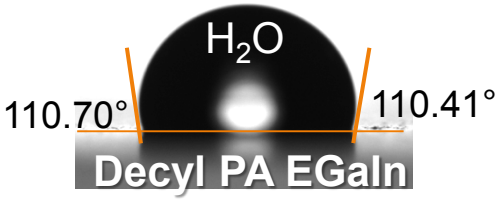


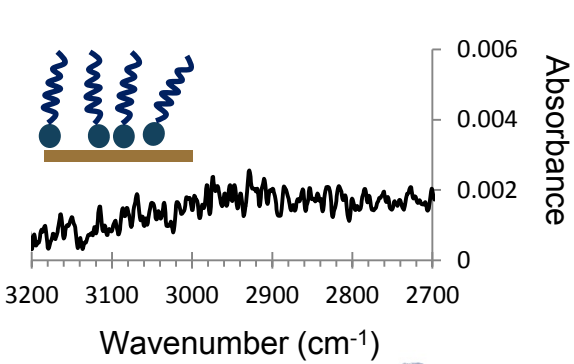
1 mM, 5 min





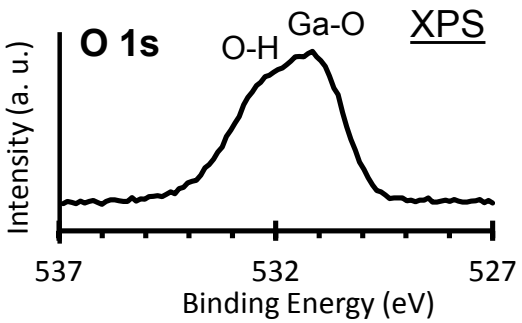
1 mM Decyl PA, 5 min
Ethanol, 30 s

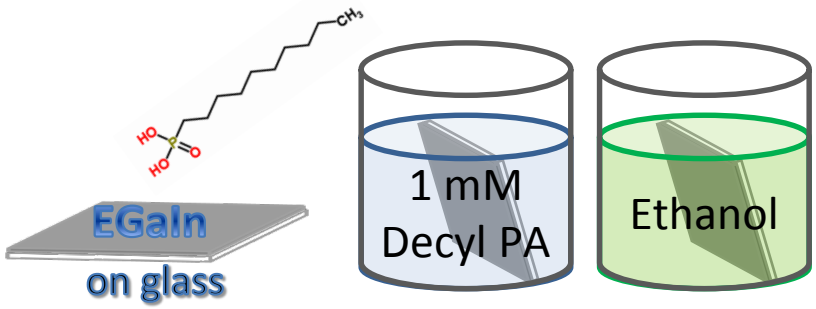




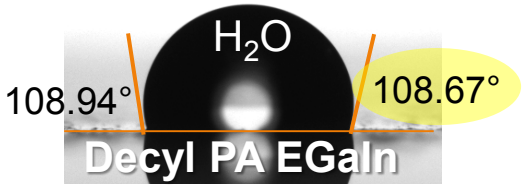
ATR-FTIR: all background subtracted

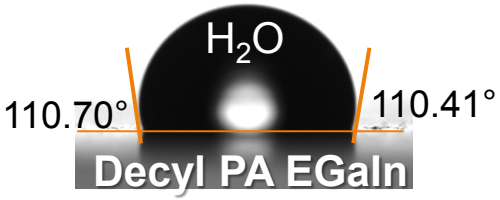
Decyl Phosphonic Acids Make the EGaIn Surface Hydrophobic





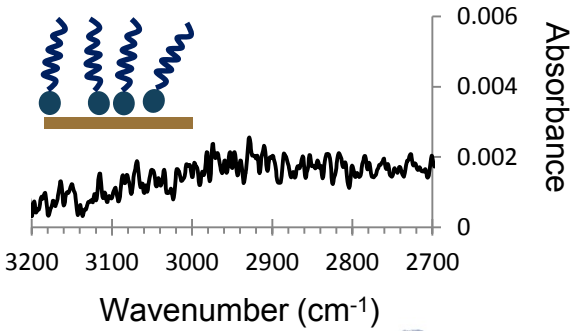
1 mM Decyl PA, 5 min
Ethanol, 30 s





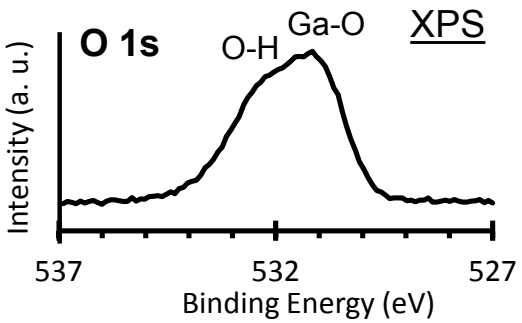
EGaIn / Decyl PA
1. 1 mM Decyl PA, 5 min
2. Ethanol, **17 hours**

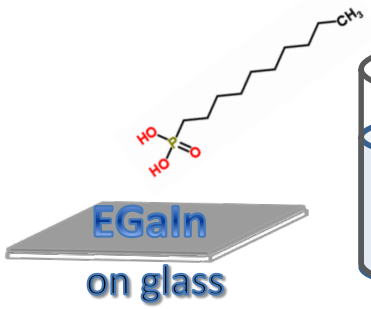
Decyl PA *strongly bound* to the surface

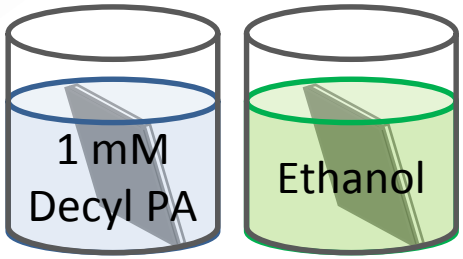


ATR-FTIR: all background subtracted

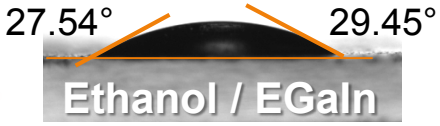
Decyl Phosphonic Acids Make the EGaIn Surface Hydrophobic

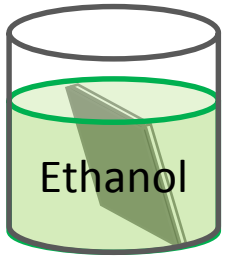






EGaIn / Decyl PA
1. 1 mM Decyl PA, 5 min
2. Ethanol, **17 hours**

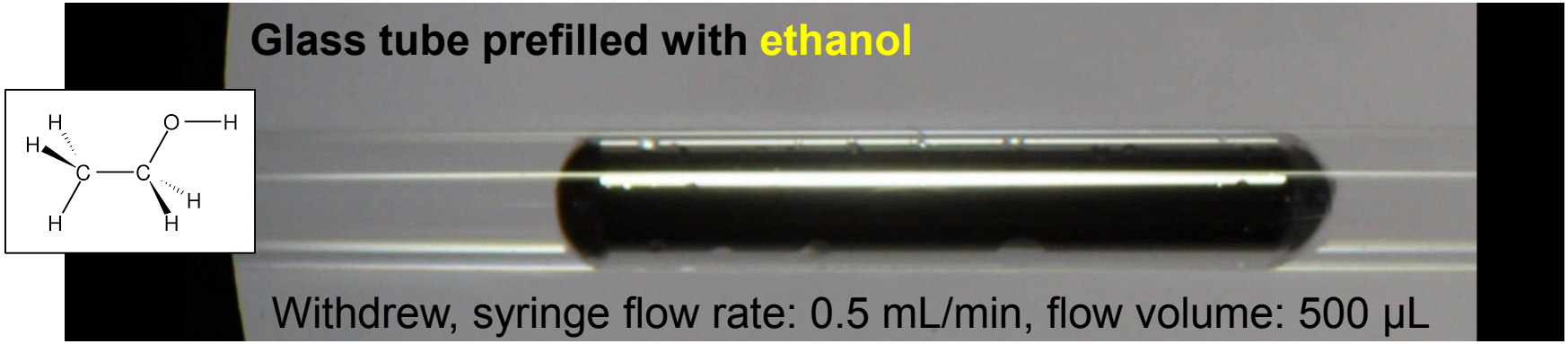


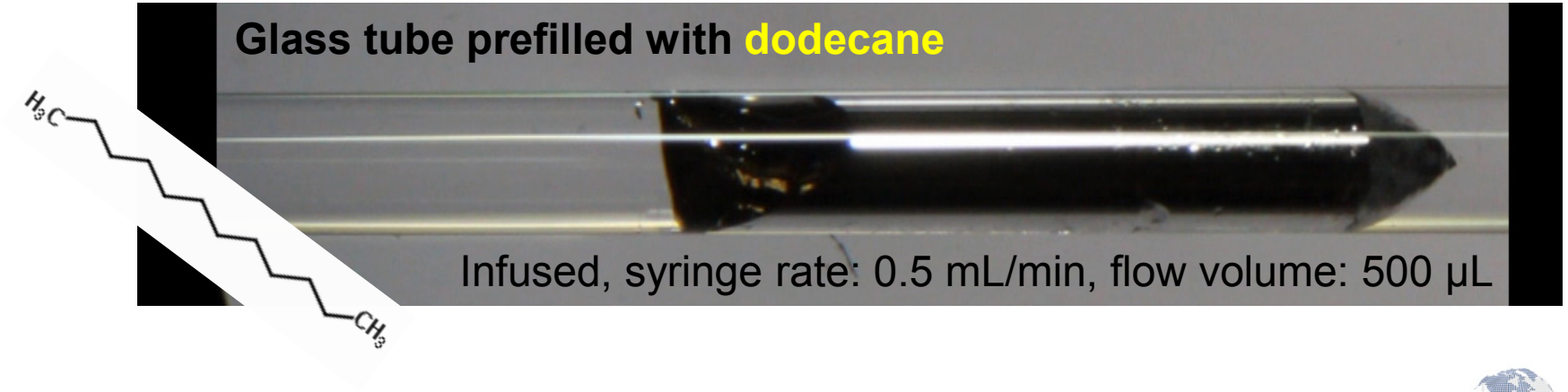


EGaIn
(No prior treatment with Decyl PA)
1. Ethanol, **23 hours**

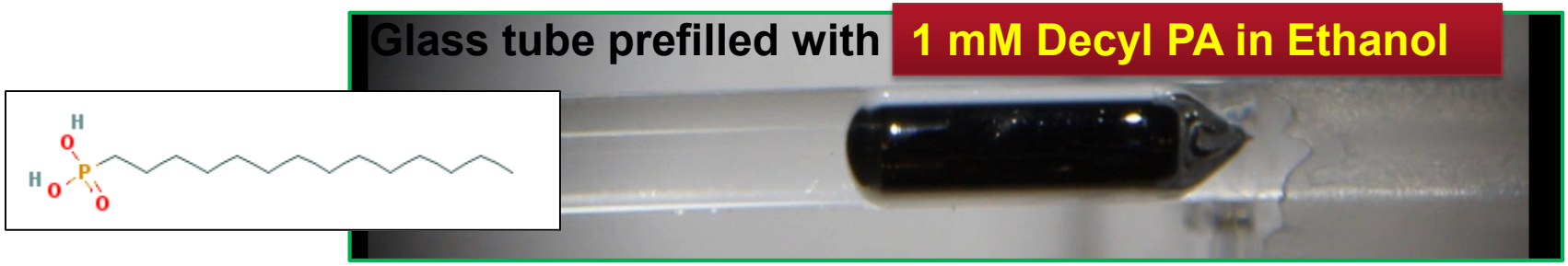
ATR-FTIR: all background subtracted

GaLMA Sticks to Glass During Injection and Flow



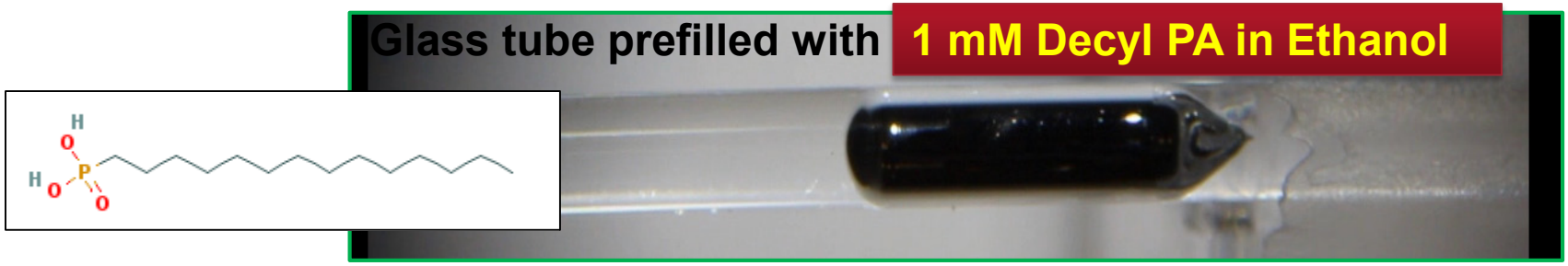


Reversible Flow of GaLMA Achieved in Decyl Phosphonic Acid Solution

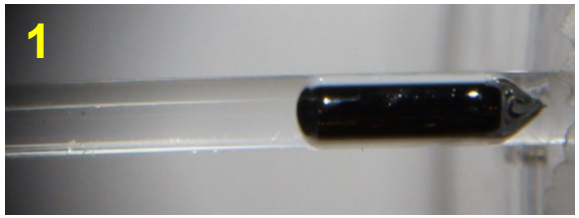


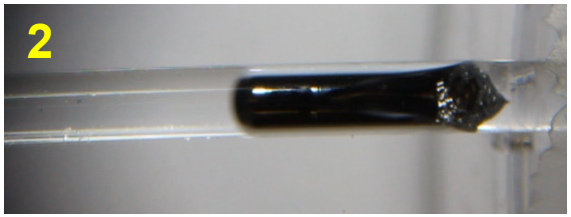
Infused, syringe rate: 2 mL/min, flow volume: 50 µL

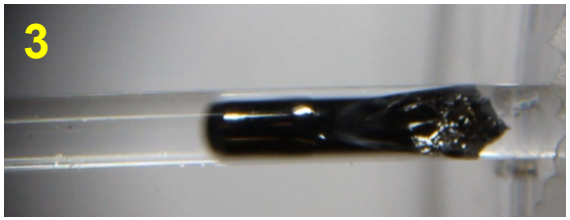
Reversible Flow of GaLMA Achieved in Decyl Phosphonic Acid Solution

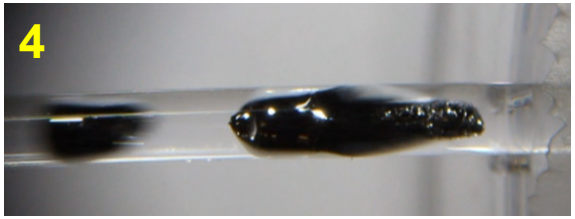


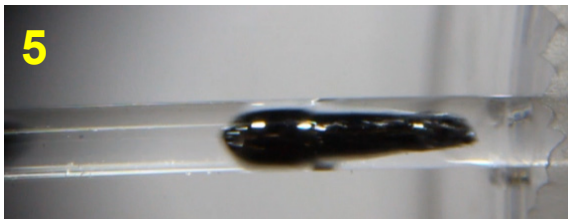
Infused, syringe rate: 2 mL/min, flow volume: 50 µL

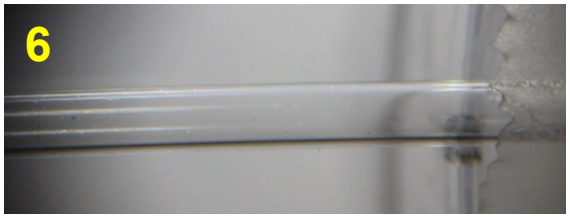






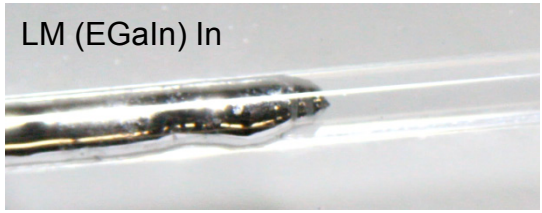


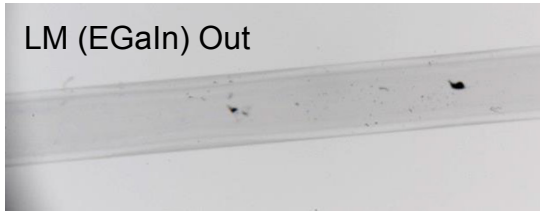


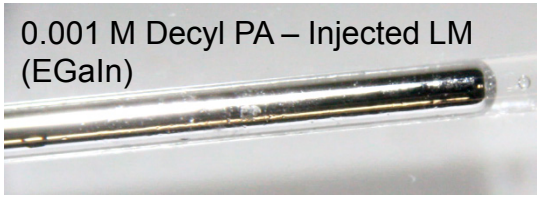


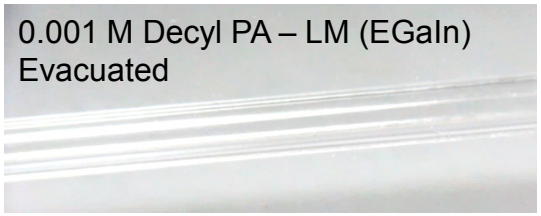
Functionalization of the Glass Tube Inner Walls vs the Surface of EGaIn

Glass Tube Pre-Treated with Decyl PA









Glass Tube Filled with Decyl PA

Infused, syringe rate: 3 mL/min, flow volume: 50 µL

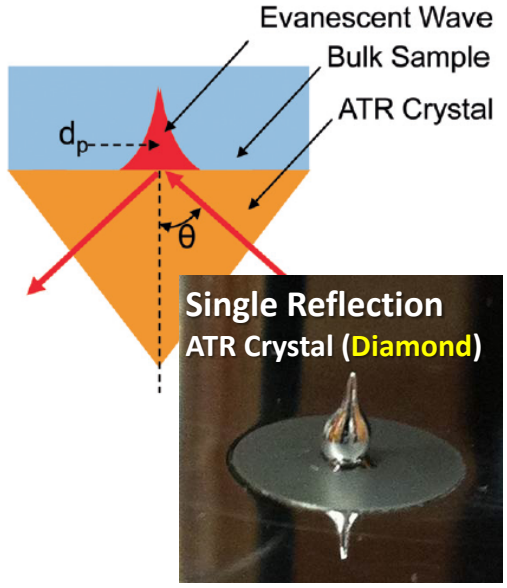
Surface Characterization
Vibrational Spectroscopy

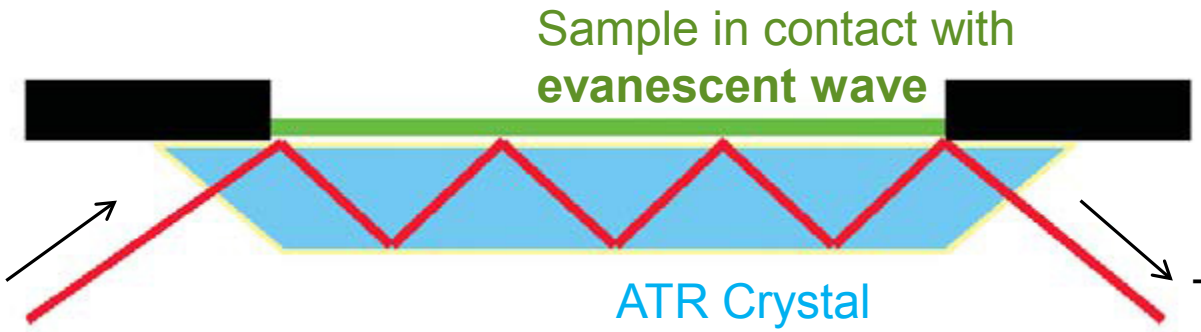
ATR-FTIR

Analysis of nanoscale thin films

Attenuated **T**otal **R**eflection

Total internal reflection at the interface when $\theta > \theta_c$





$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right) \qquad E = E_0 e^{-\left(\frac{z}{d_p}\right)}$$

$$n_1 > n_2 \qquad d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2\theta - n_2^2}}$$

Evanescent wave: standing wave due to the superposition of incident and reflected waves

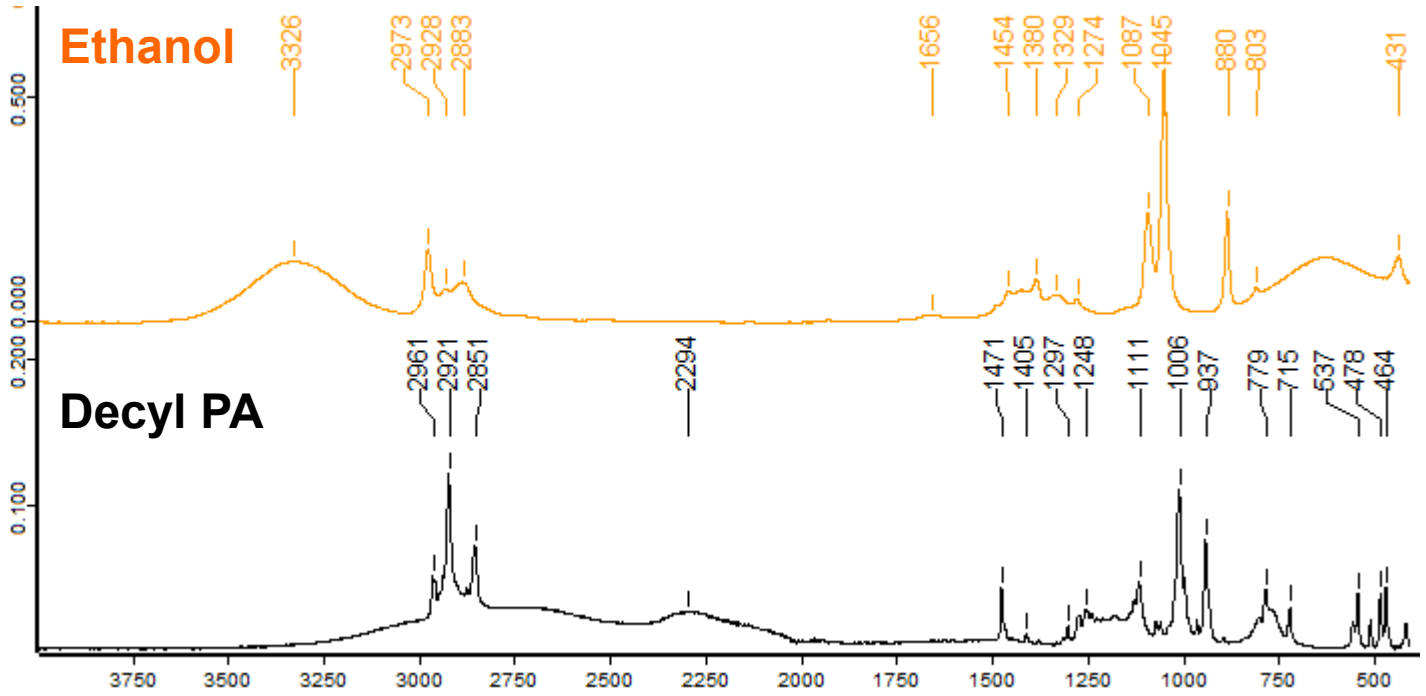
E: Amplitude of standing electric wave
E_0: Amplitude at the interface (z=0)
z: Distance from the interface
d_p: Penetration depth
θ: Incidence angle
n_1, n_2: Refractive Indices
λ: Wavelength of the radiation

Image taken from Bruker Catalog

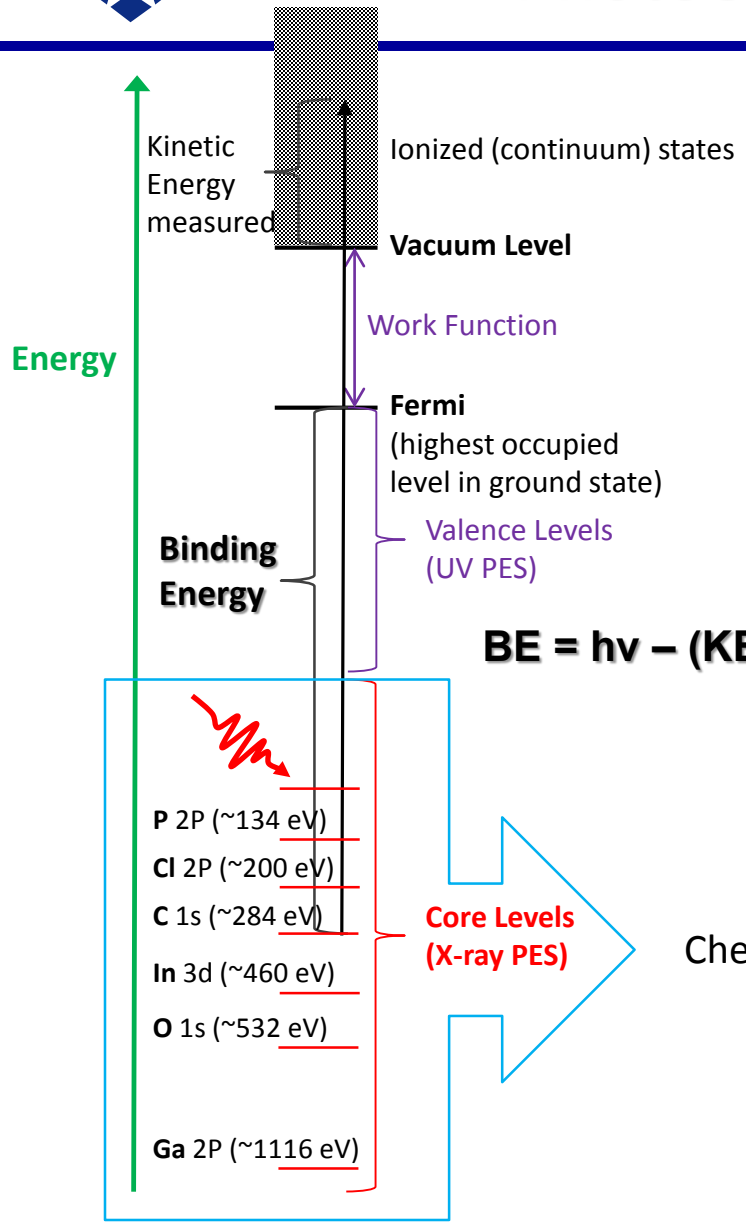
Surface Characterization
Vibrational Spectroscopy

ATR-FTIR

- Sensitive to thin films
- Our setup is not sensitive for monolayer films (need sensitive detectors/reflection methods
- **Sufficient to study thin film formation dynamics**

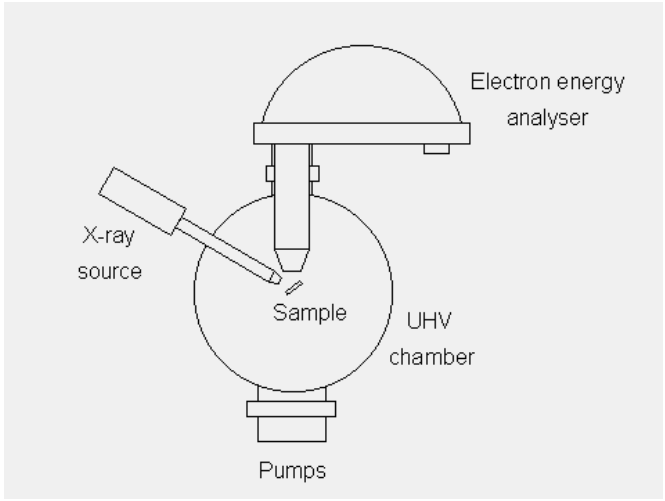


Surface Characterization
Photoelectron Spectroscopy



BE = hv – (KE + WF)

Photoelectron Spectrometer



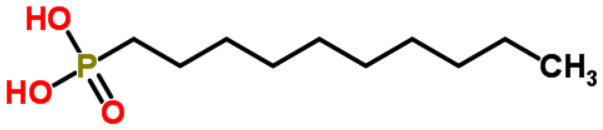
http://www.chem.qmul.ac.uk/surfaces/scc/scat5_3.htm

XPS

Binding energy (BE) depends on:

1. Formal oxidation state of the atom
2. Local chemical environment

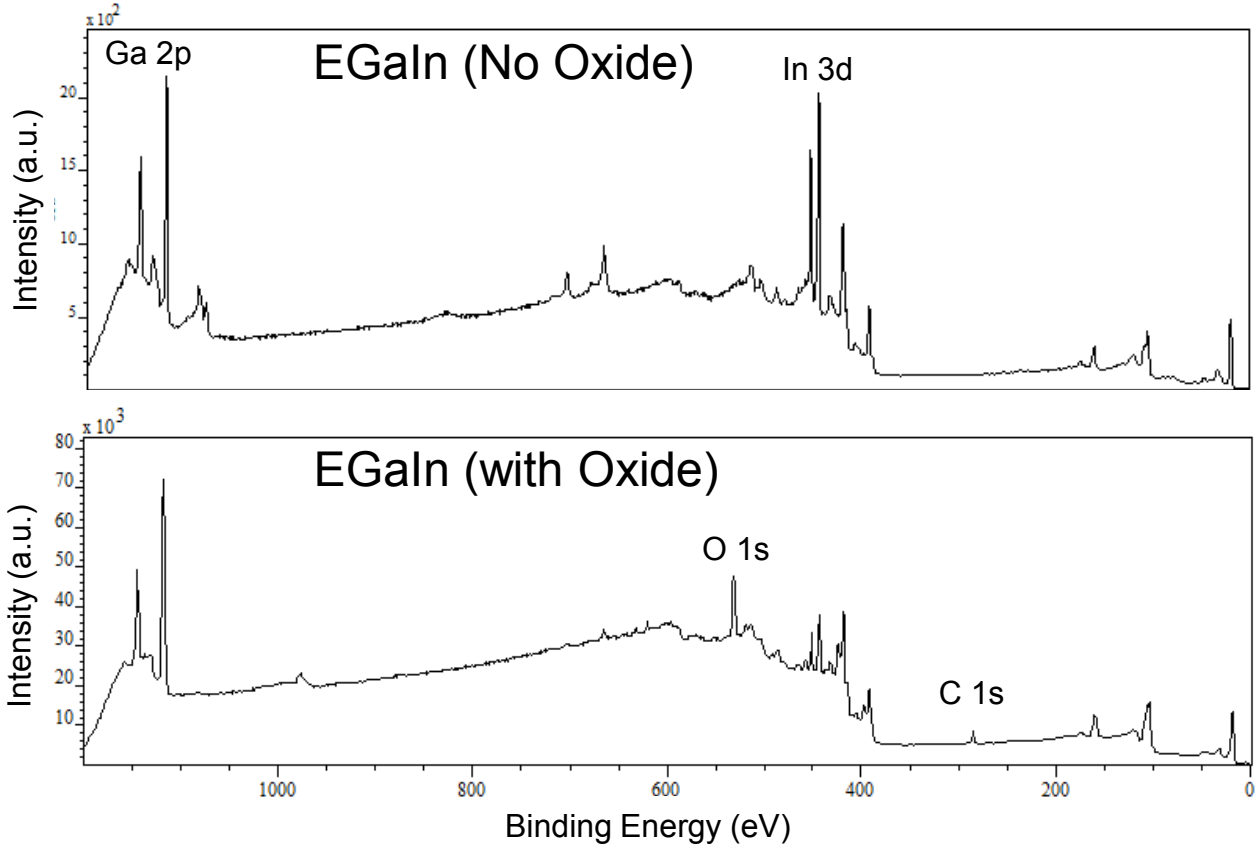
Chemical/elemental analysis of alkyl phosphonic acids on **EGaIn**

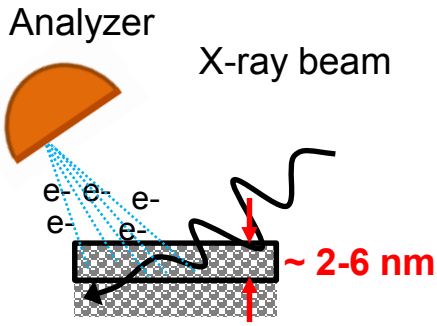


Surface Characterization
Photoelectron Spectroscopy

XPS

- X-Ray Photoelectron Spectroscopy
- Sensitive to submonolayers (parts per thousand)
- Our setup: sampling depth of ~2-6 nm
- **Quantitative/chemical information for elemental analysis**

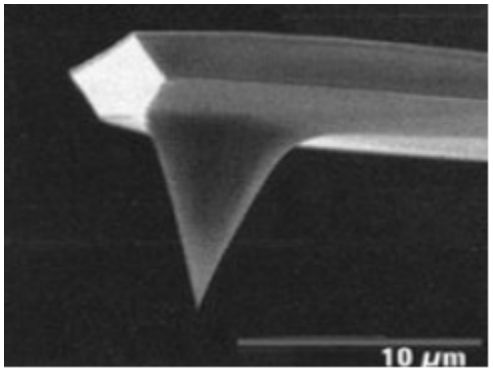


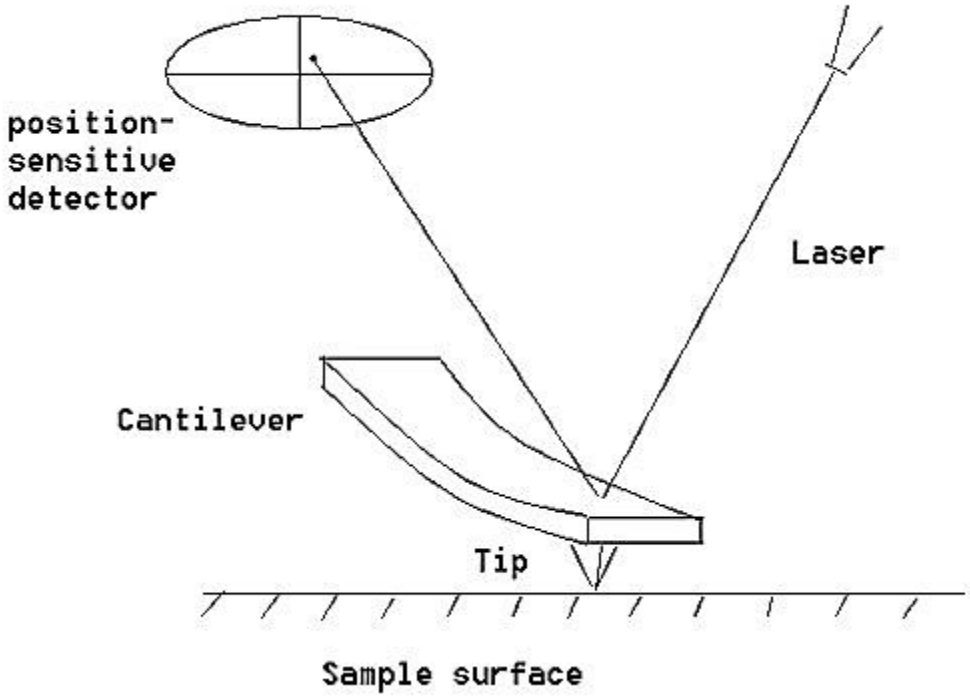


Surface Characterization
Atomic Force Microscopy

AFM

- Excellent vertical resolution up to 1 Å
- Later resolution generally not as good





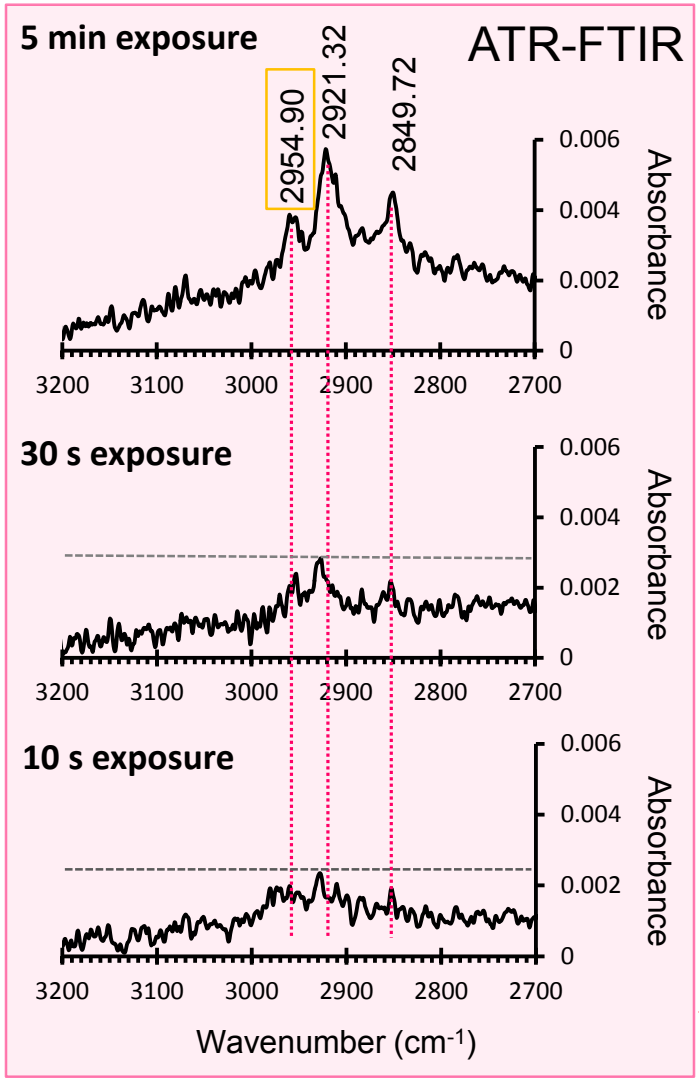
Contact Mode | Non-Contact Mode | Tapping Mode

deflection | attractive vdW | oscillation amplitude

http://www.nanoscience.gatech.edu/zlwang/research/afm.html
http://www.physik.uni-greifswald.de/scientific-groups/helm/methods/afm-atomic-force-microscope.html?L=1

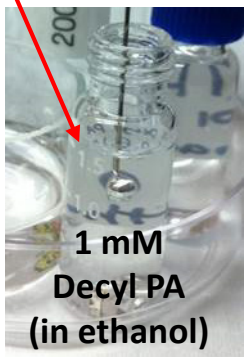
Surface Coverage is a Dynamic Process

Surface Film Coverage Increases with Adsorption Time

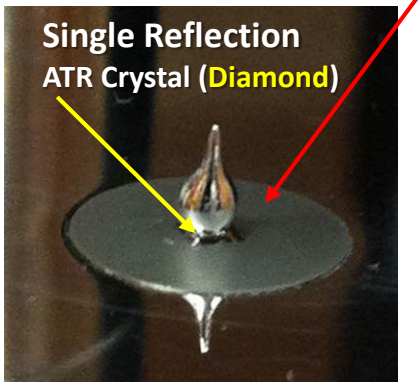


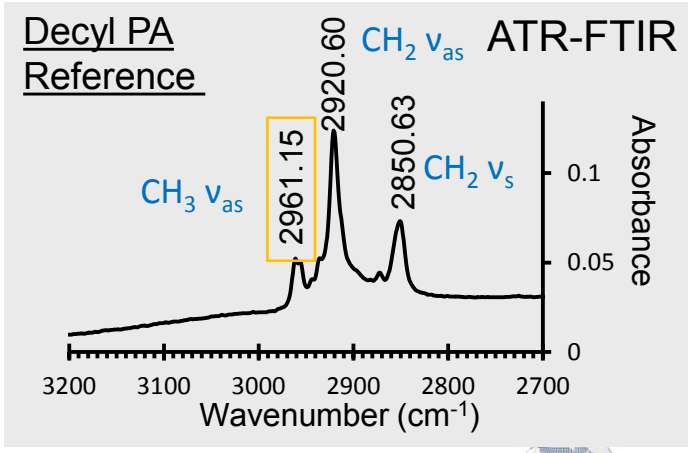
EGaIn background subtracted

LM injected into the PA solution & suspended



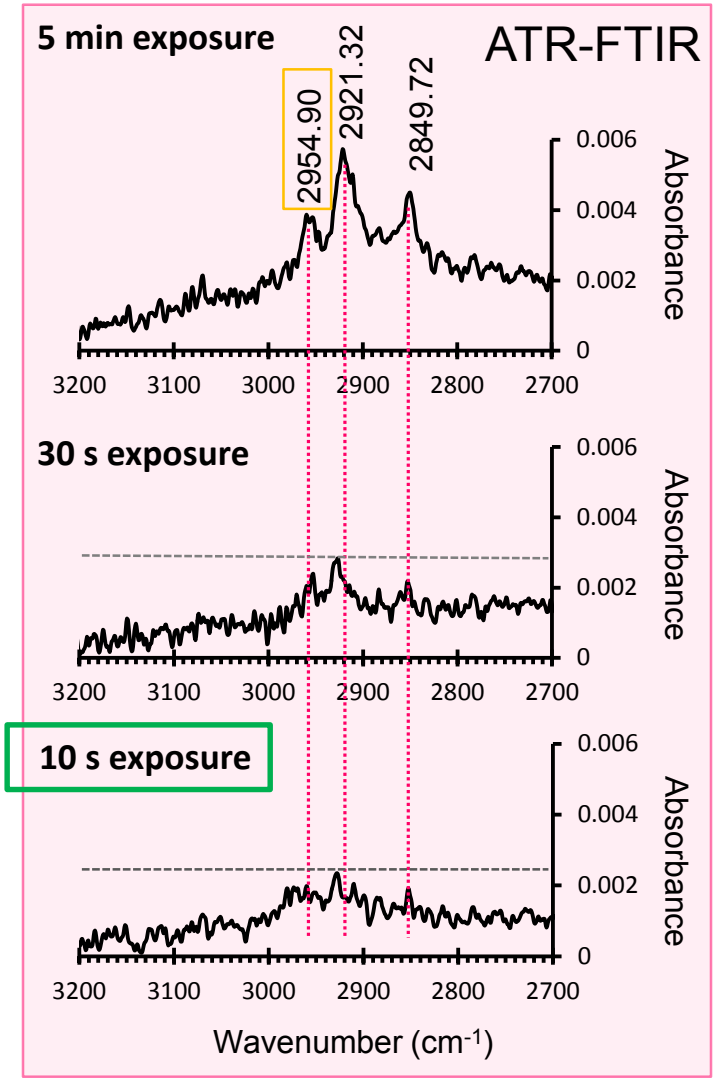
ATR-FTIR – gently placed the suspended droplet onto ATR crystal

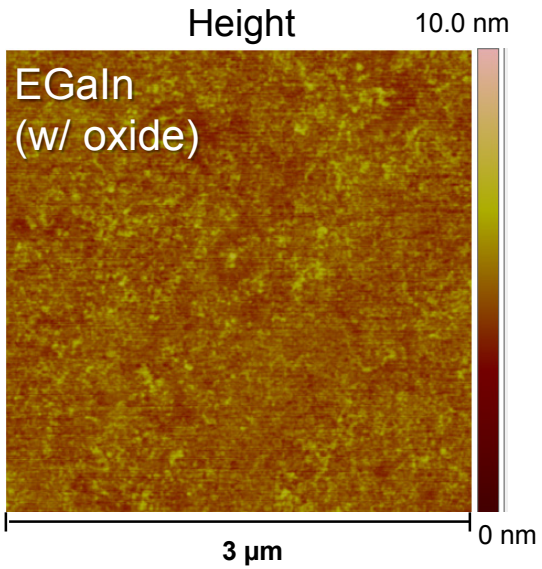


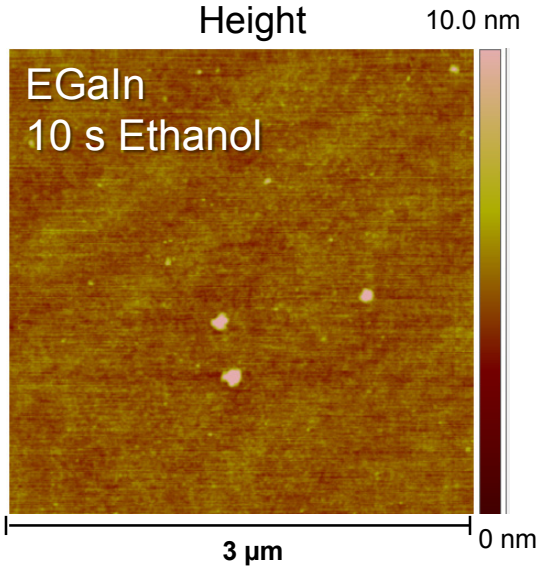


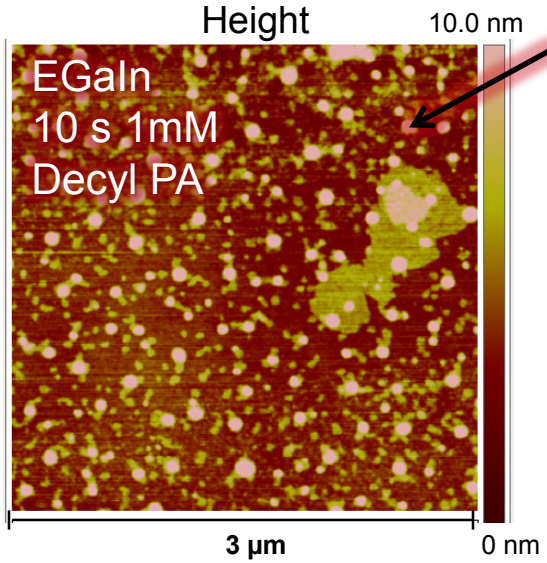
Surface Coverage is a Dynamic Process

ATR-FTIR/AFM - Growth mode: 3D islands

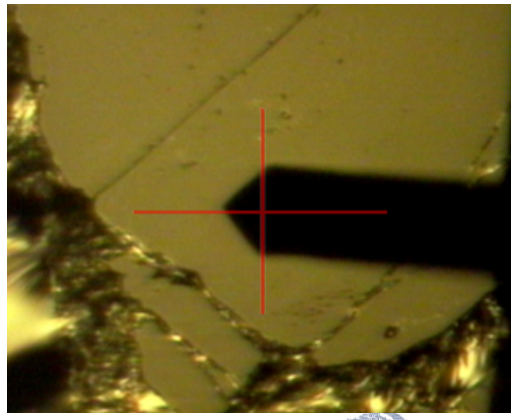






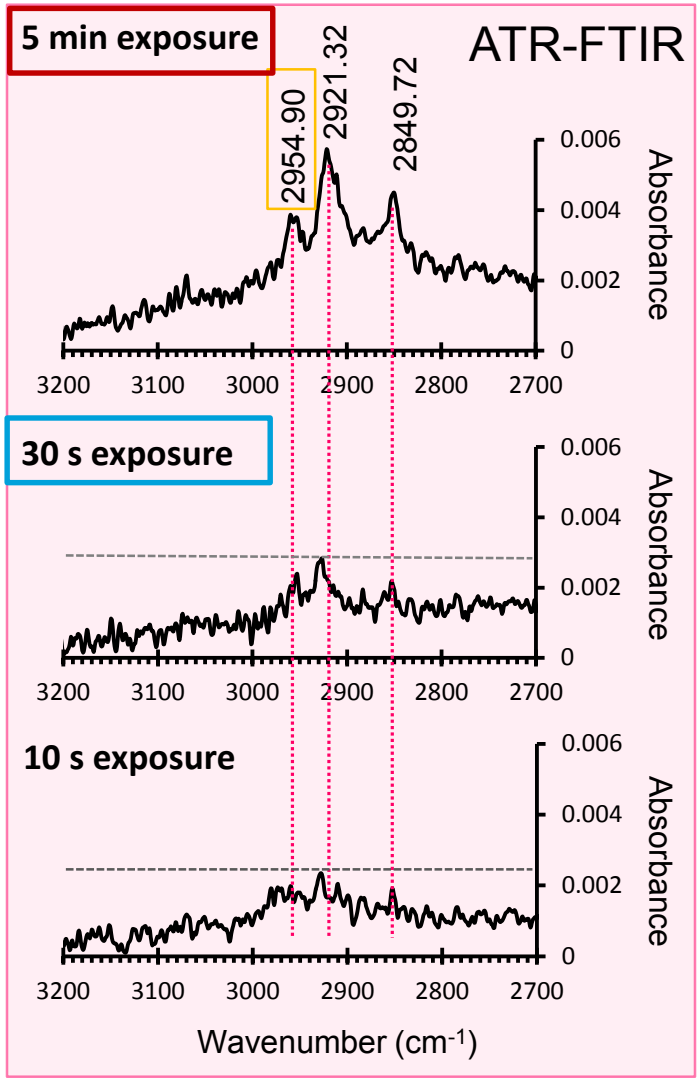


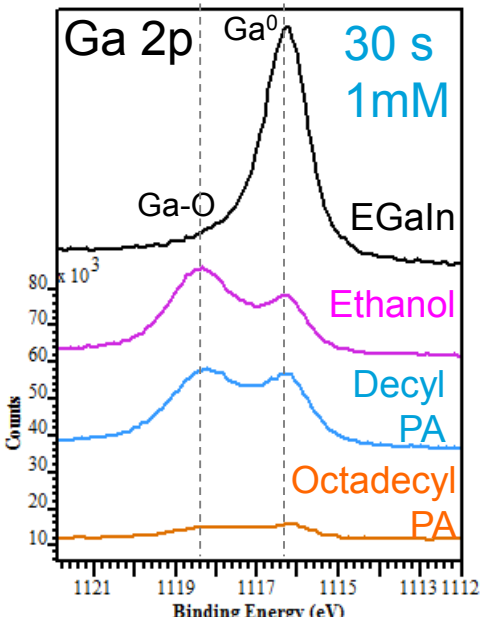
The onset of Island formation

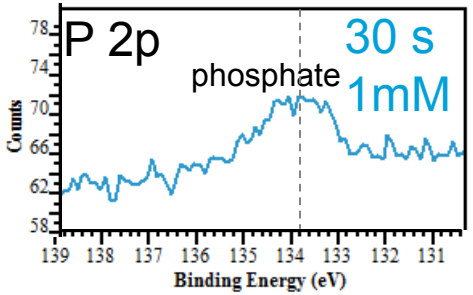


Surface Coverage is a Dynamic Process

ATR-FTIR/XPS - Growth mode: 3D islands







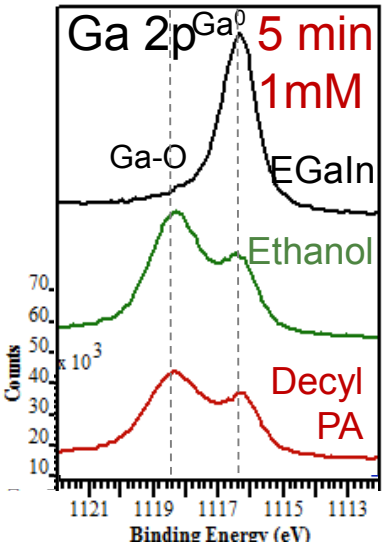
Atomic Composition

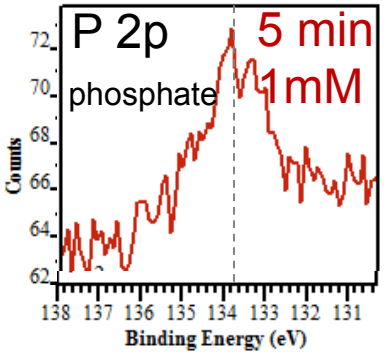
Ga/P = 5.5

Ga/O = 0.8

C/P = 7.9 (10)

O/P = 7.0 (3)





Atomic Composition

Ga/P = 5.4

Ga/O = 0.8

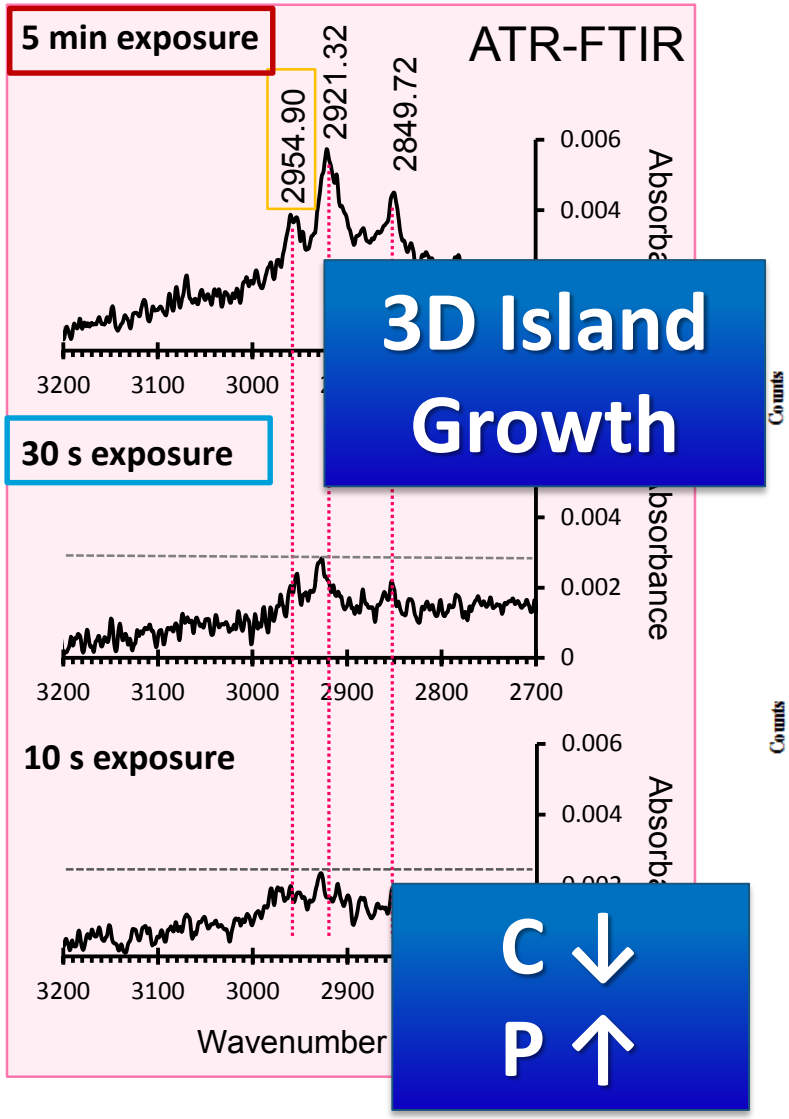
C/P = 6.7 (10)

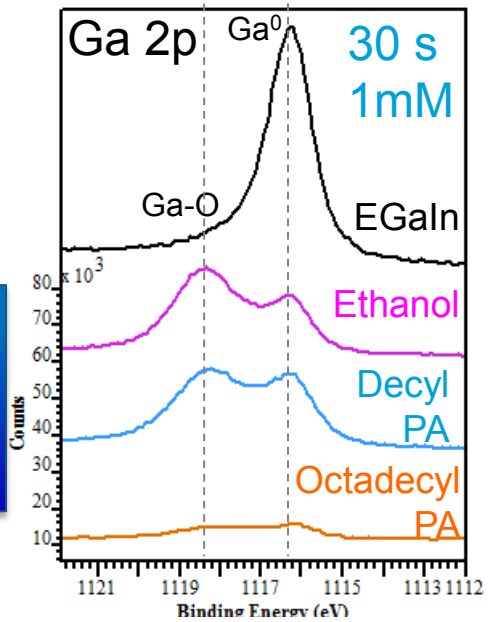
O/P = 6.8 (3)

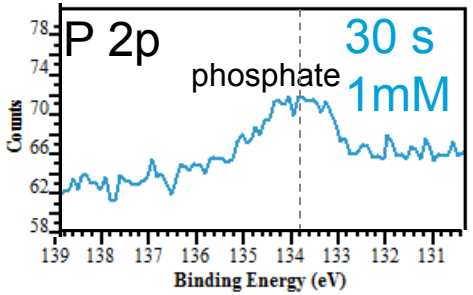
Our XPS setup: sampling depth of ~2-6 nm

Surface Coverage is a Dynamic Process

Surface Film Coverage Increases with Adsorption Time







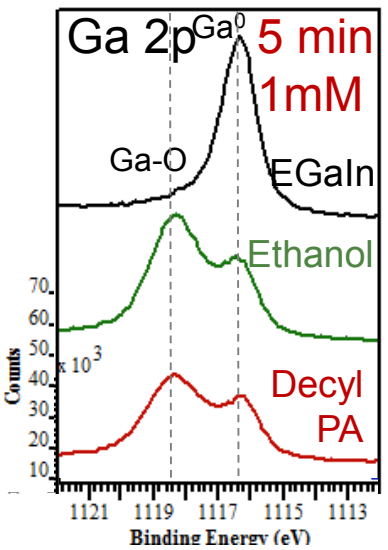
Atomic Composition

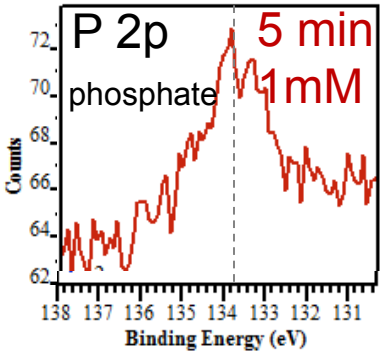
Ga/P = 5.5

Ga/O = 0.8

C/P = 7.9 (10)

O/P = 7.0 (3)





Atomic Composition

Ga/P = 5.4

Ga/O = 0.8

C/P = 6.7 (10)

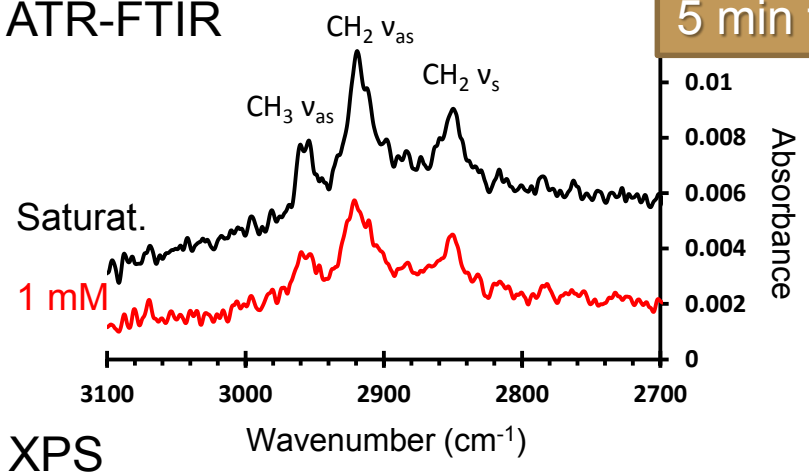
O/P = 6.8 (3)

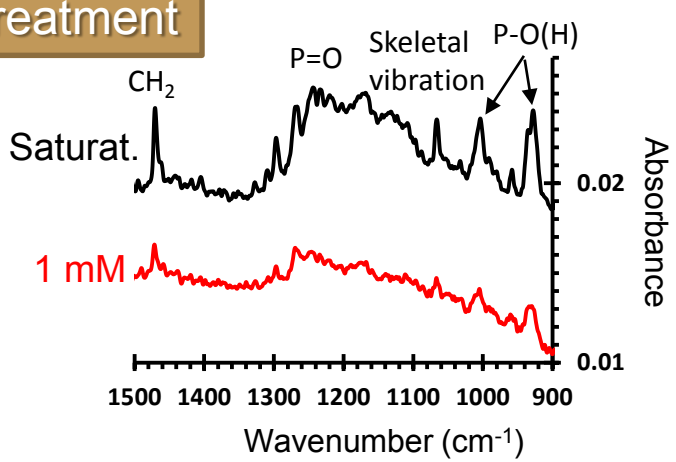
Our XPS setup: sampling depth of ~2-6 nm

Film Growth- Adsorption Rate of Decyl PA Increases with Solution Concentration

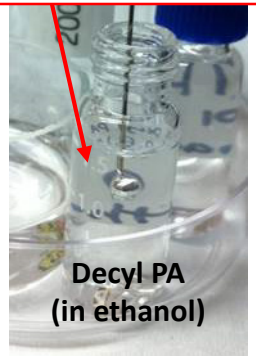
ATR-FTIR

5 min treatment

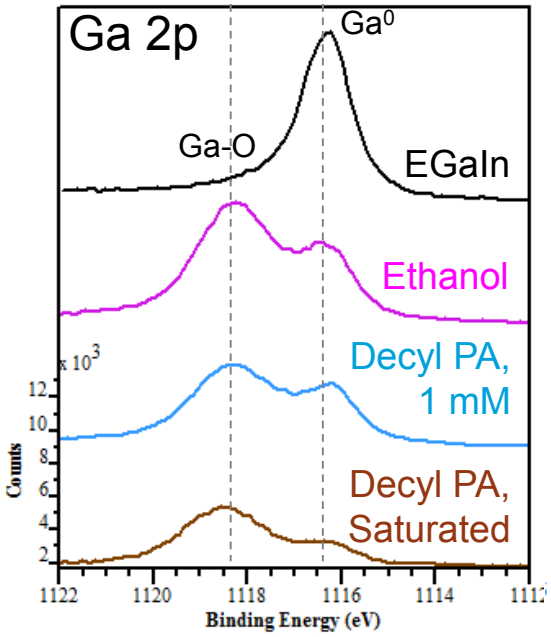


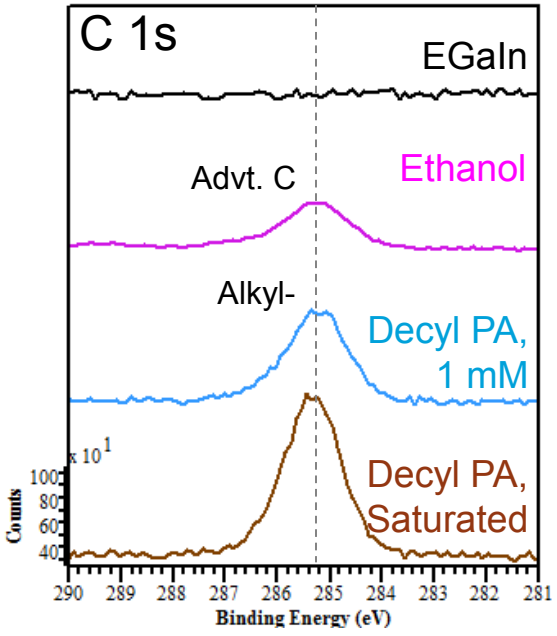


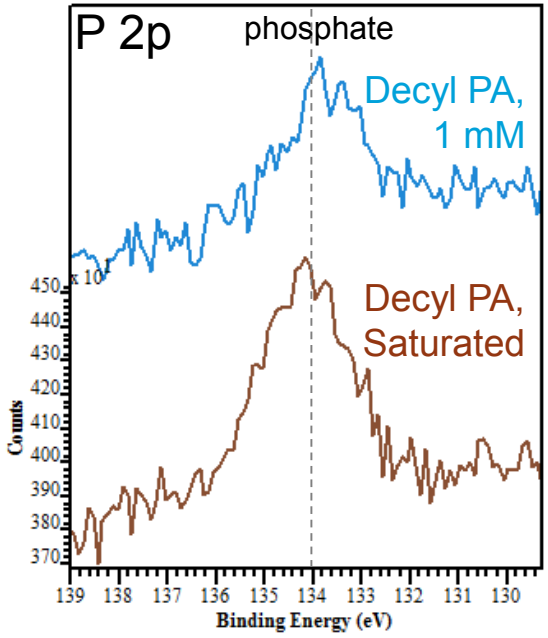
LM injected into the PA solution & suspended: 5 min



XPS

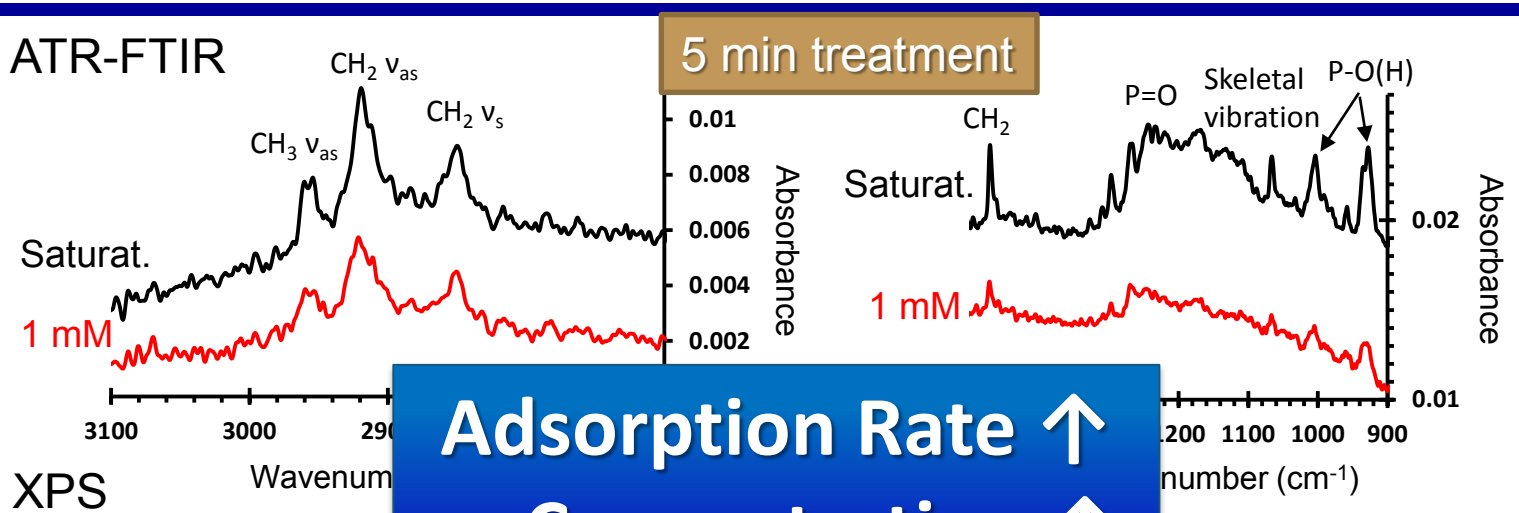






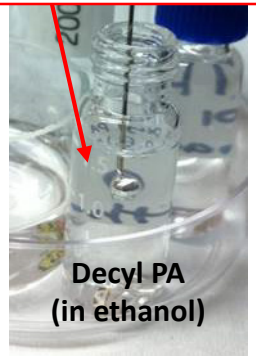
Our XPS setup: sampling depth of ~2-6 nm

Film Growth- Adsorption Rate of Decyl PA Increases with Solution Concentration

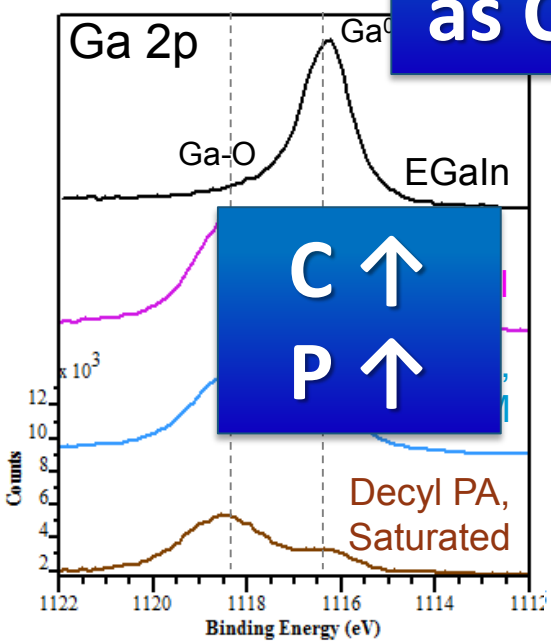


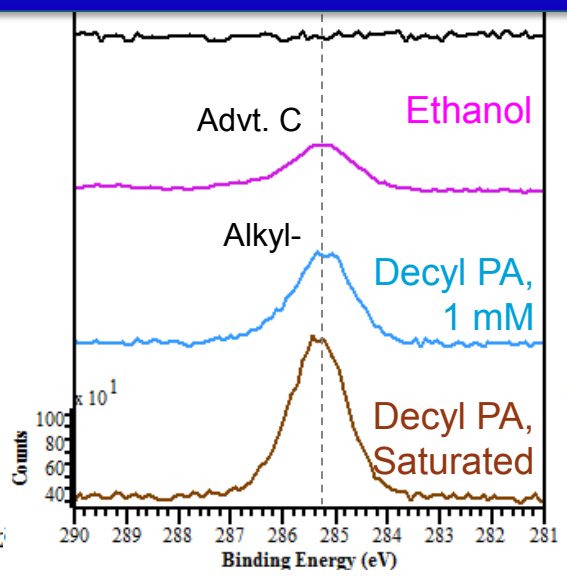
Adsorption Rate ↑ as Concentration ↑

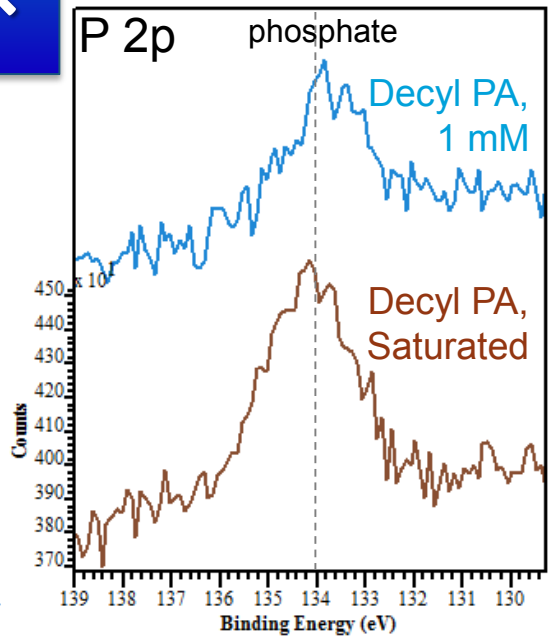
LM injected into the PA solution & suspended: 5 min



XPS

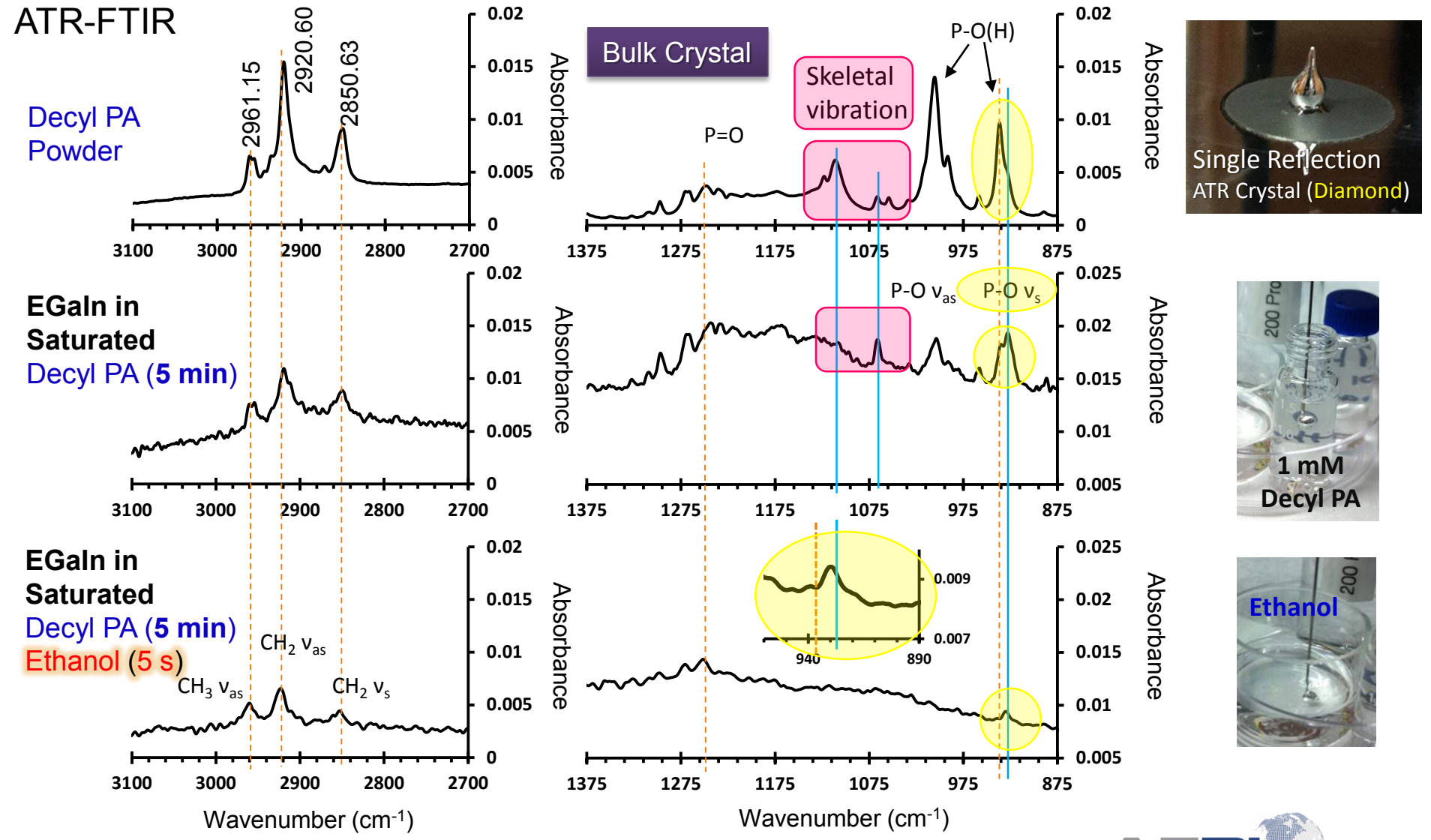






Our XPS setup: sampling depth of ~2-6 nm

Thin Film Structure
Bulk Crystalline vs Thin Film

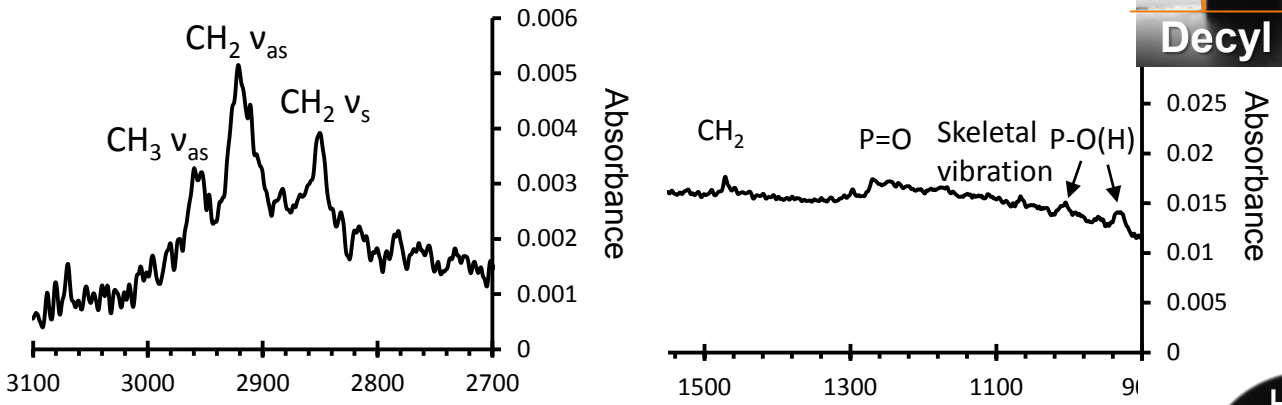


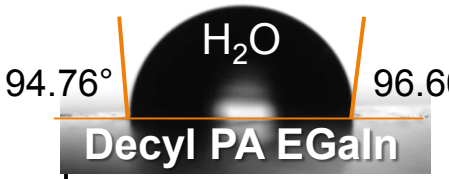
PA-Functionalized EGaIn

Film Coverage Decreases upon Rinsing with Ethanol

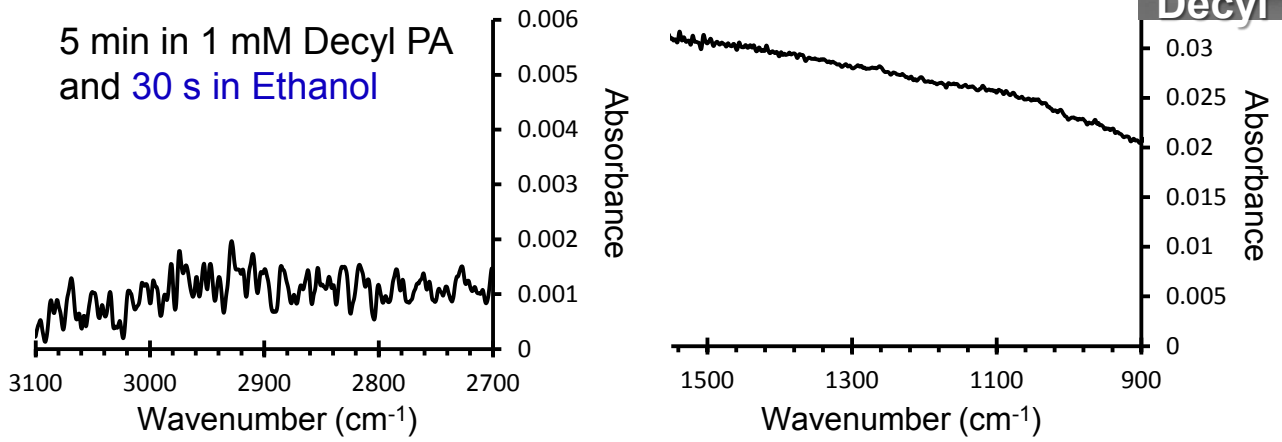
ATR-FTIR

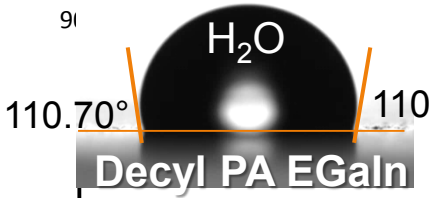
5 min in 1 mM Decyl PA





5 min in 1 mM Decyl PA + 30 s Ethanol



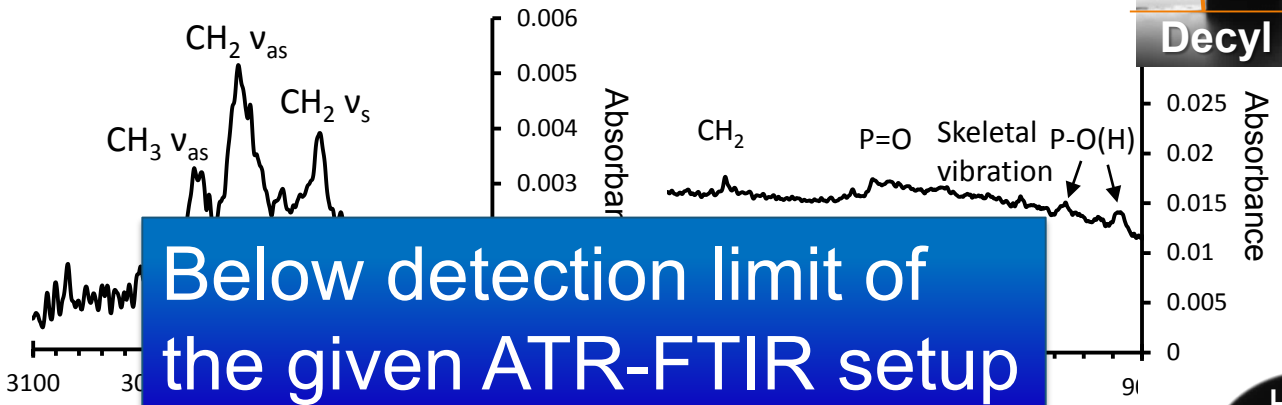


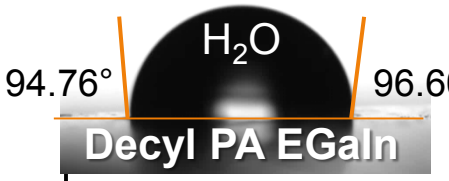
PA-Functionalized EGaIn

Film Coverage Decreases upon Rinsing with Ethanol

ATR-FTIR

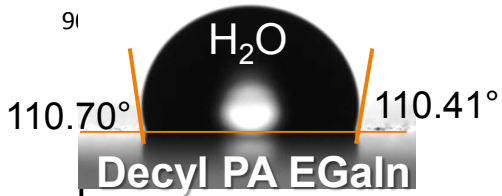
5 min in 1 mM Decyl PA

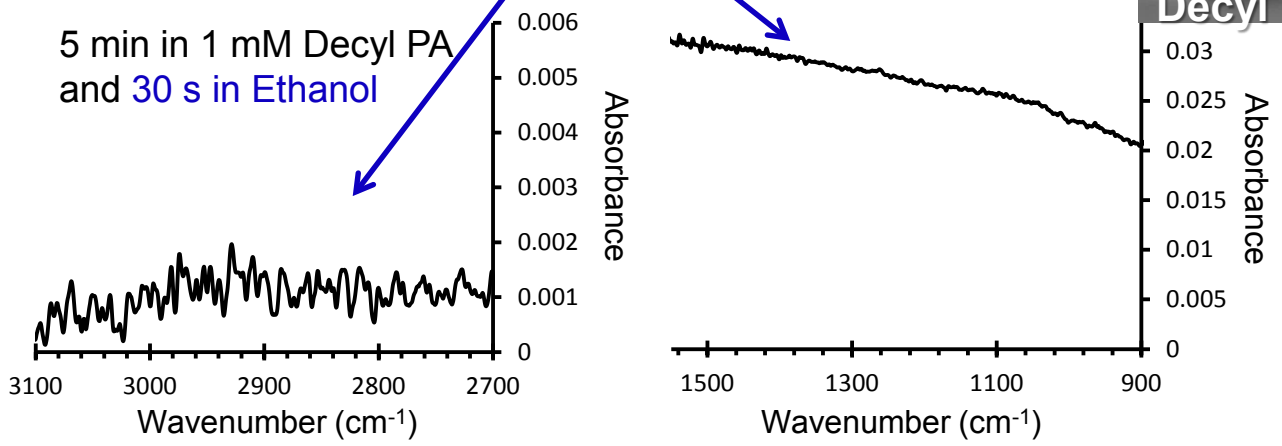




Below detection limit of the given ATR-FTIR setup

5 min in 1 mM Decyl PA + 30 s Ethanol





PA-Functionalized EGaIn

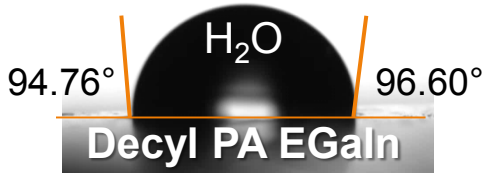
Film Coverage Decreases upon Rinsing with Ethanol

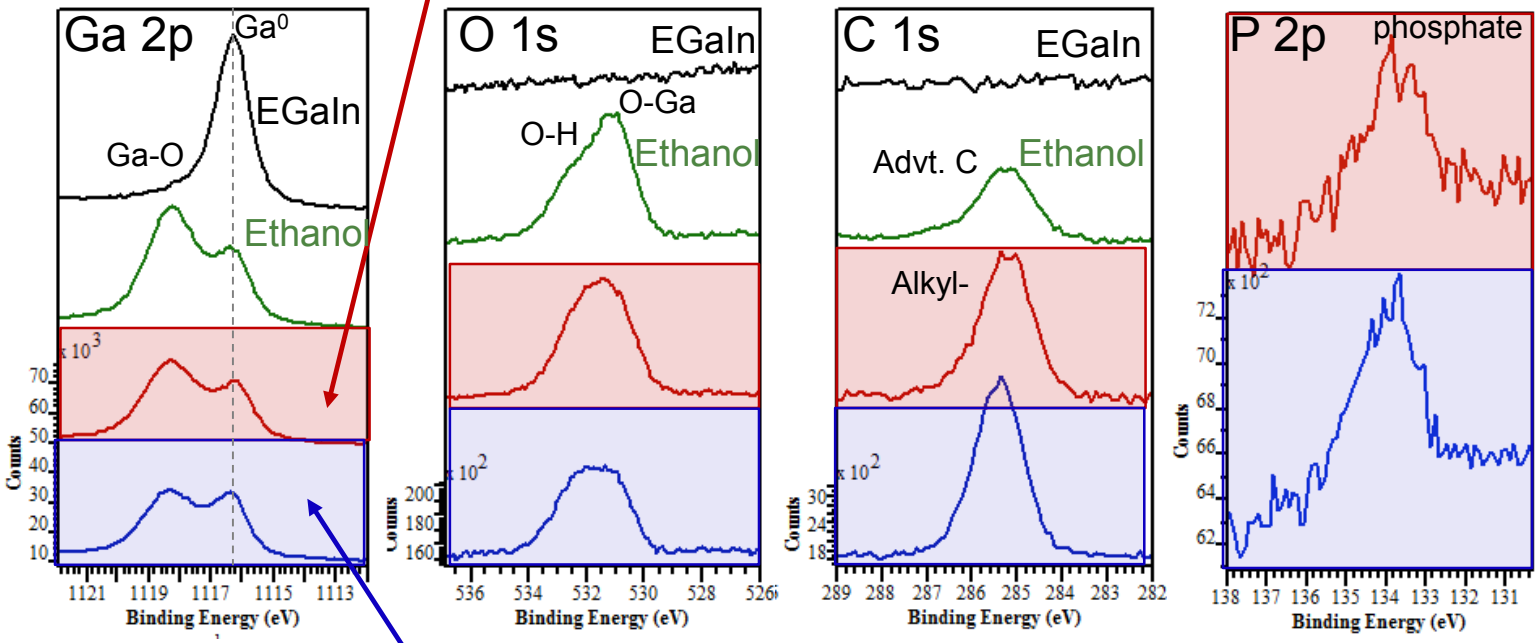
XPS

5 min in 1 mM Decyl PA

Atomic Composition

Ga/P = 5.4 Ga/O = 0.8 C/P = 6.7 (10) O/P = 6.8 (3)

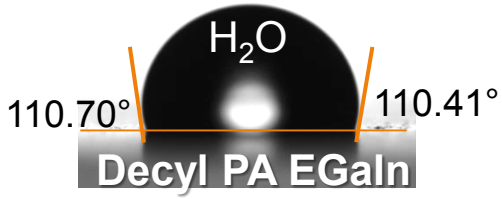




5 min in 1 mM Decyl PA + 30 s Ethanol

Atomic Composition

Ga/P = 5.9 Ga/O = 1.1 C/P = 6.9 (10) O/P = 5.6 (3)



Our XPS setup: sampling depth of ~2-6 nm

PA-Functionalized EGaIn

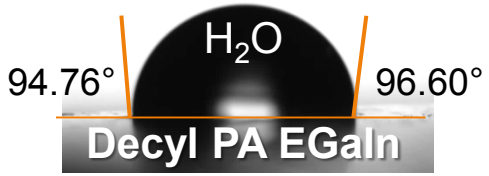
Film Coverage Decreases upon Rinsing with Ethanol

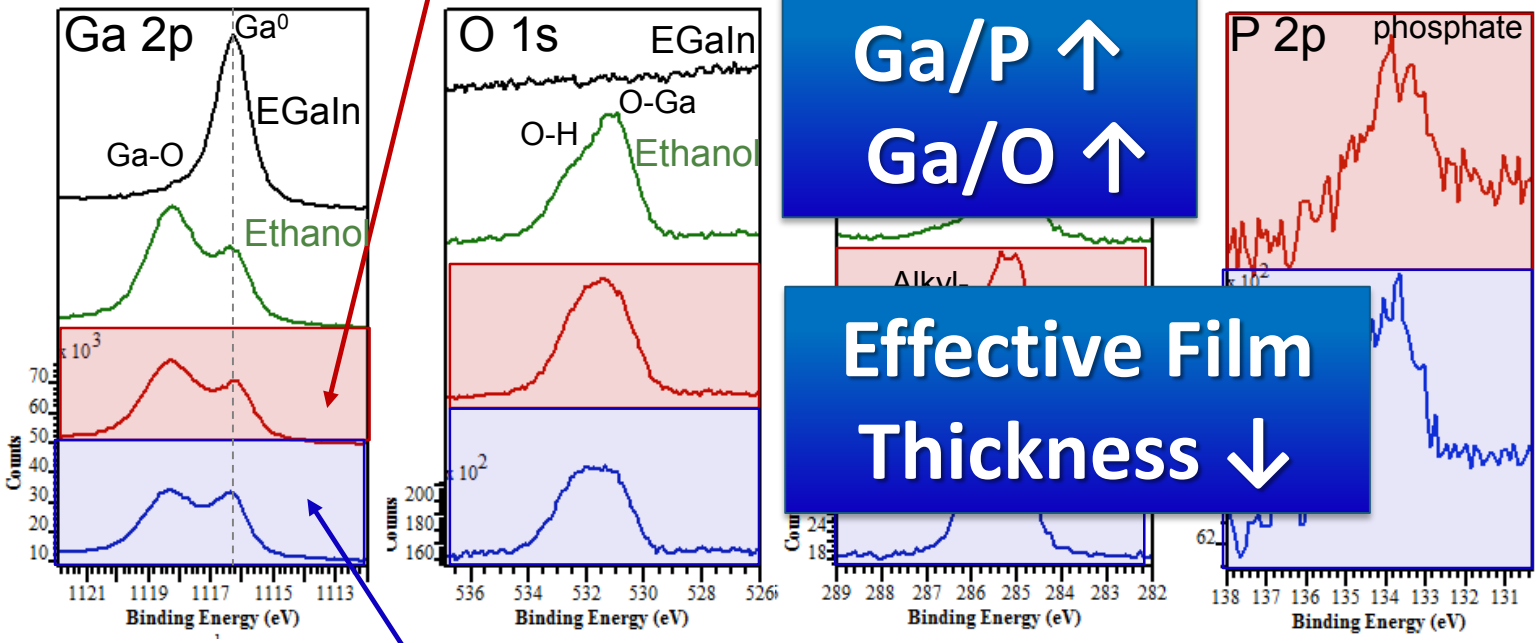
XPS

5 min in 1 mM Decyl PA

Atomic Composition

Ga/P = 5.4 Ga/O = 0.8 C/P = 6.7 (10) O/P = 6.8 (3)





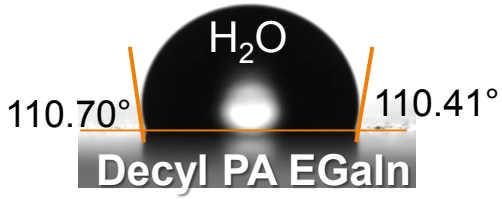
Ga/P ↑
Ga/O ↑

Effective Film Thickness ↓

5 min in 1 mM Decyl PA + 30 s Ethanol

Atomic Composition

Ga/P = 5.9 Ga/O = 1.1 C/P = 6.9 (10) O/P = 5.6 (3)



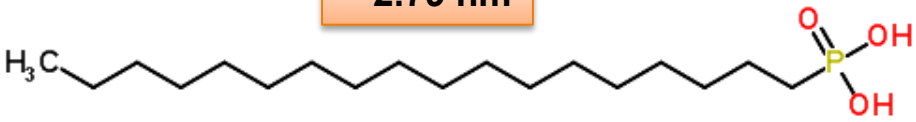
Our XPS setup: sampling depth of ~2-6 nm

Effects of Alkyl Chain Length

Decyl (10 carbons) PA *vs* Octadecyl (18 carbons) PA

~ 1.72 nm

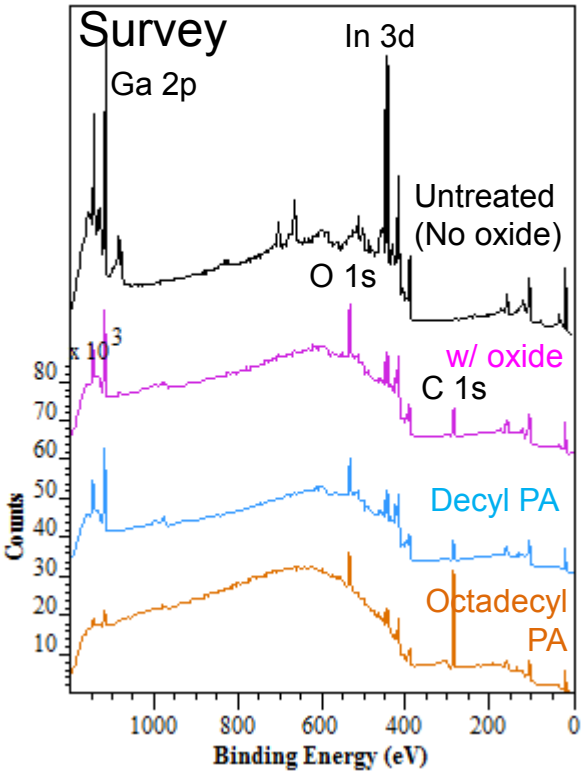
~ 2.79 nm

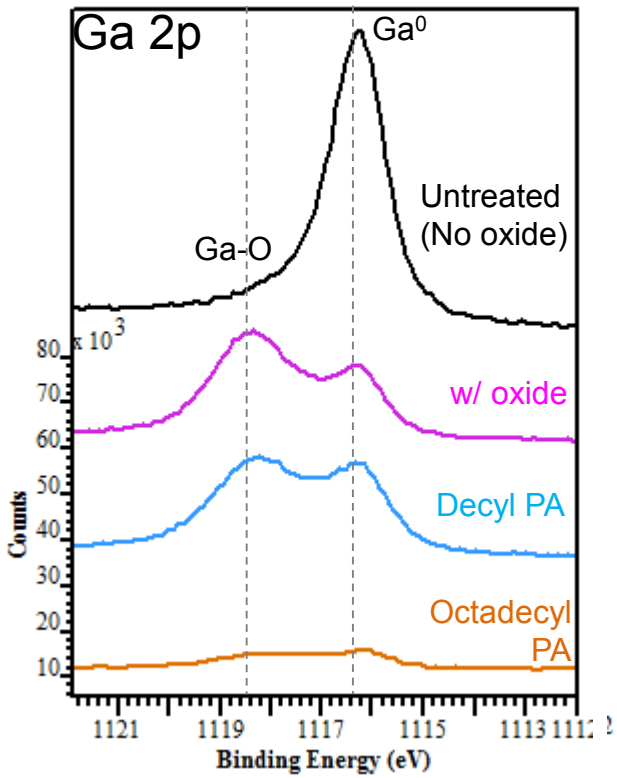


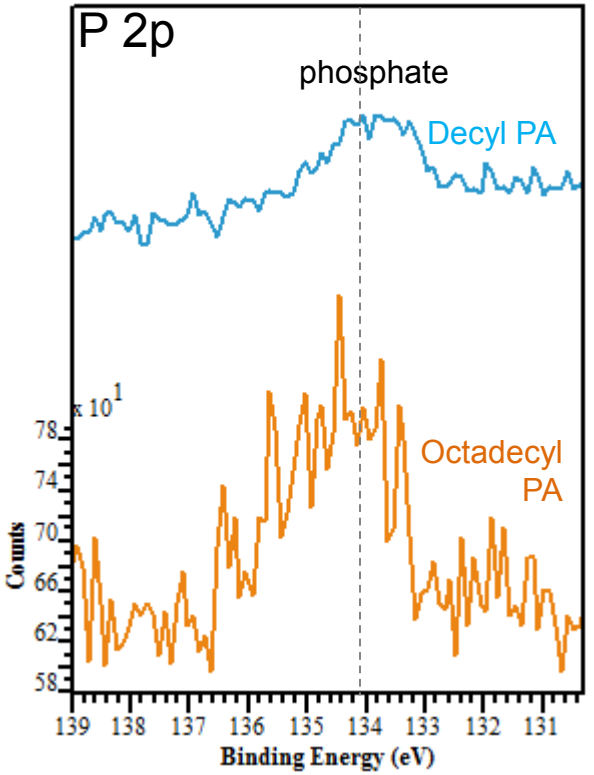
Atomic Composition

XPS

Decyl PA	Ga/P = 5.5	Ga/O = 0.8	C/P = 8.0	(10)	O/P = 7.0	(3)
Octadecyl PA	Ga/P = 0.8	Ga/O = 0.1	C/P = 22.2	(10)	O/P = 5.1	(3)







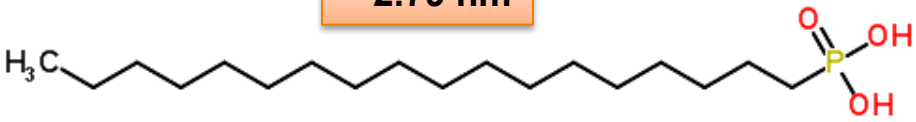
Our XPS setup: sampling depth of ~2-6 nm

Effects of Alkyl Chain Length

Decyl (10 carbons) PA *vs* Octadecyl (18 carbons) PA

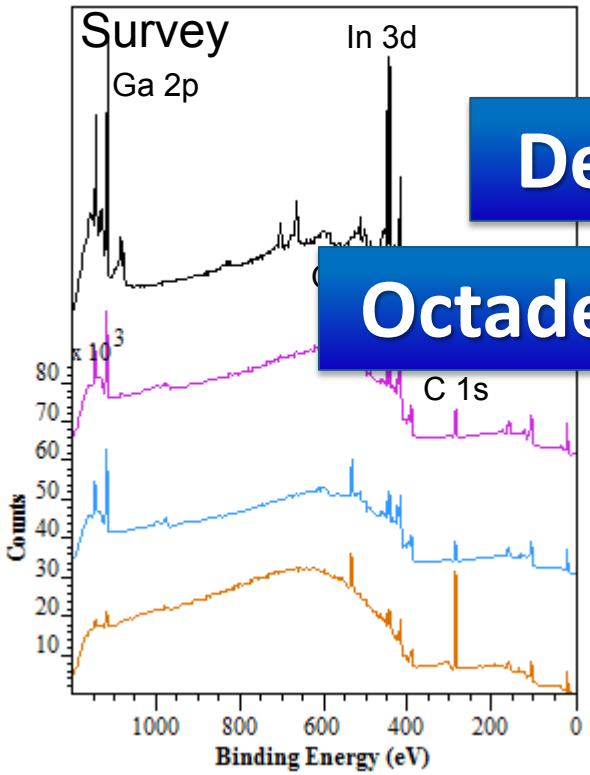
~ 1.72 nm

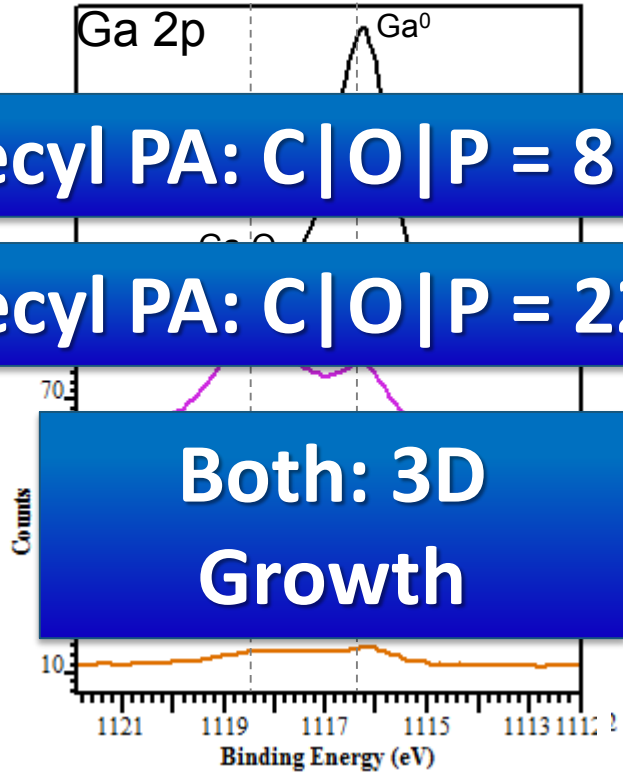
~ 2.79 nm

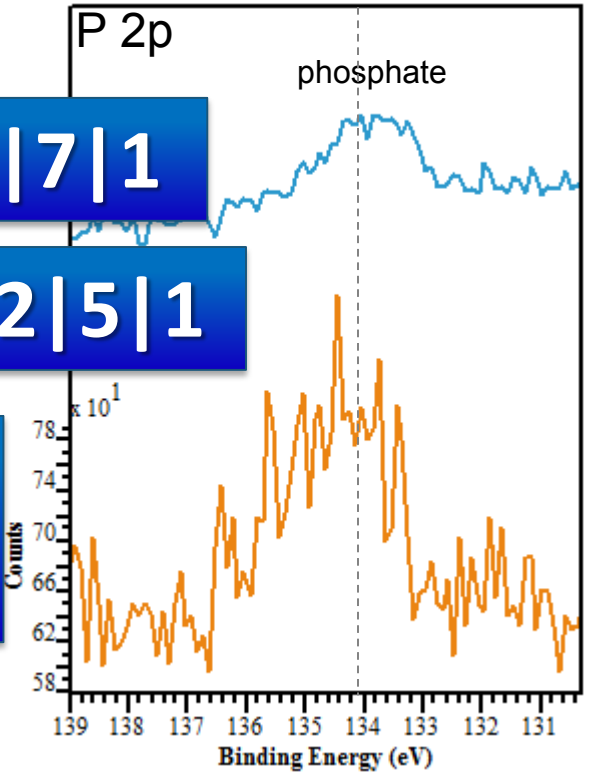


Atomic Composition

Decyl PA	Ga/P = 5.5	Ga/O = 0.8	C/P = 8.0	(10)	O/P = 7.0	(3)
Octadecyl PA	Ga/P = 0.8	Ga/O = 0.1	C/P = 22.2	(10)	O/P = 5.1	(3)







Decyl PA: C|O|P = 8|7|1

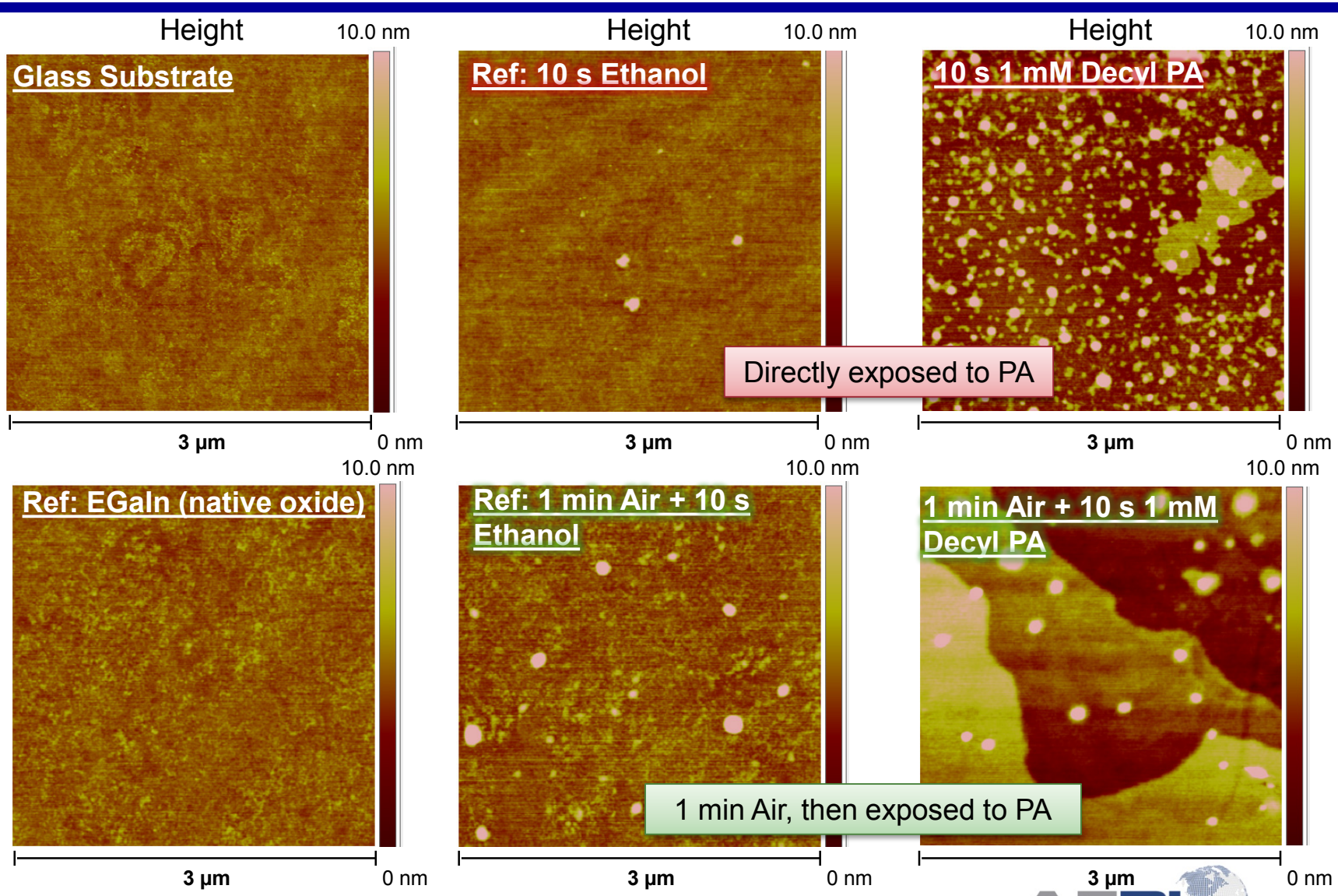
Octadecyl PA: C|O|P = 22|5|1

Both: 3D Growth

Our XPS setup: sampling depth of ~2-6 nm

Decyl Phosphonic Acid – Film Structure

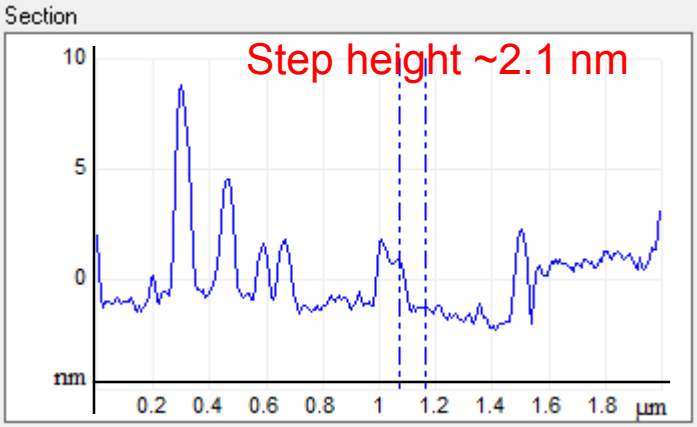
Effects of the Surface Oxide on Film Formation



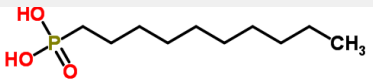
Decyl Phosphonic Acid – Film Structure

Effects of the Surface Oxide on Film Formation

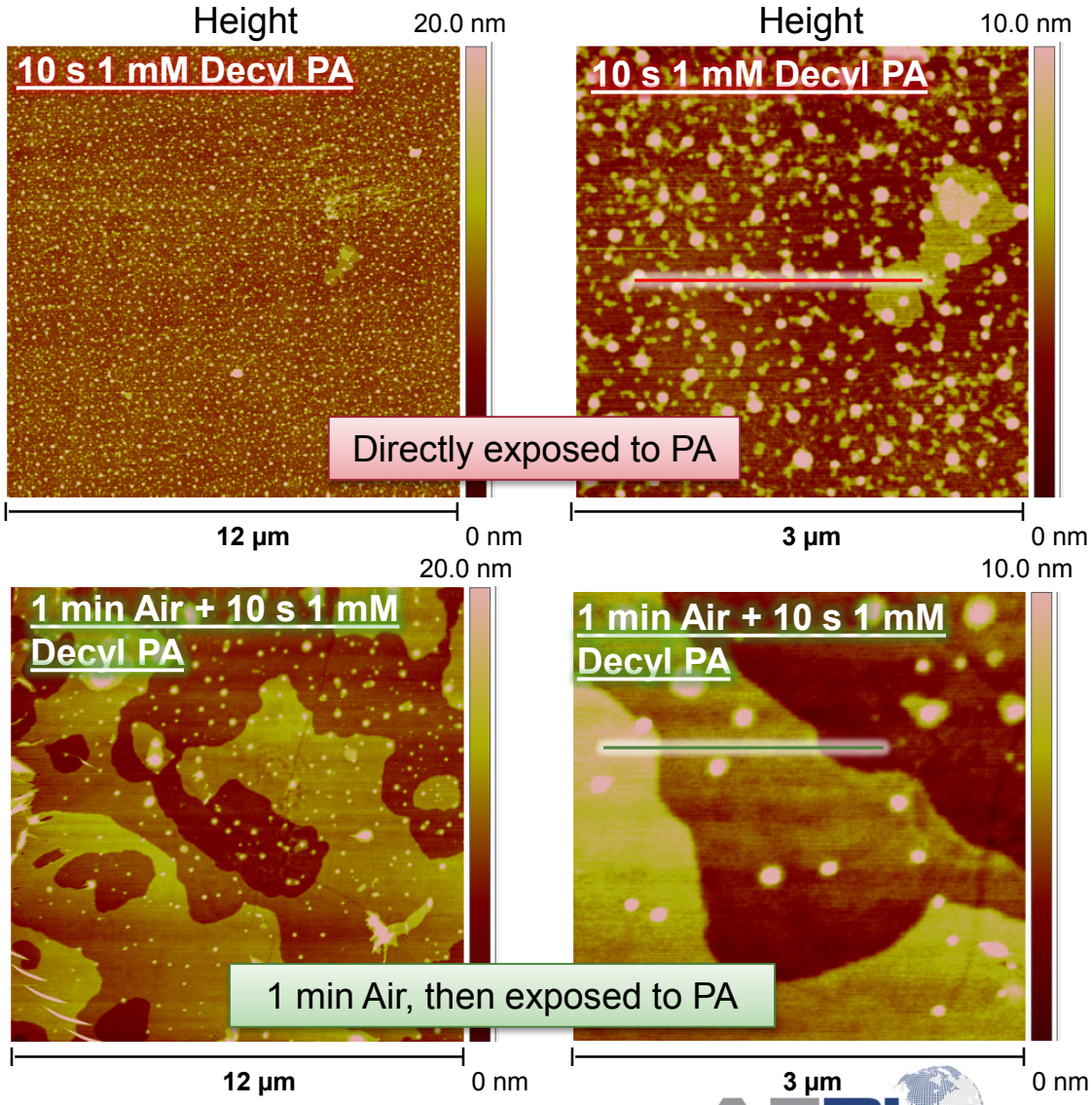
Directly exposed to PA



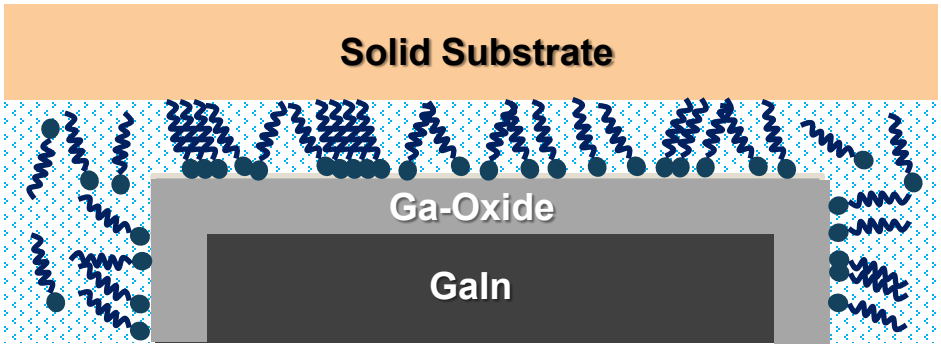
~ 1.72 nm



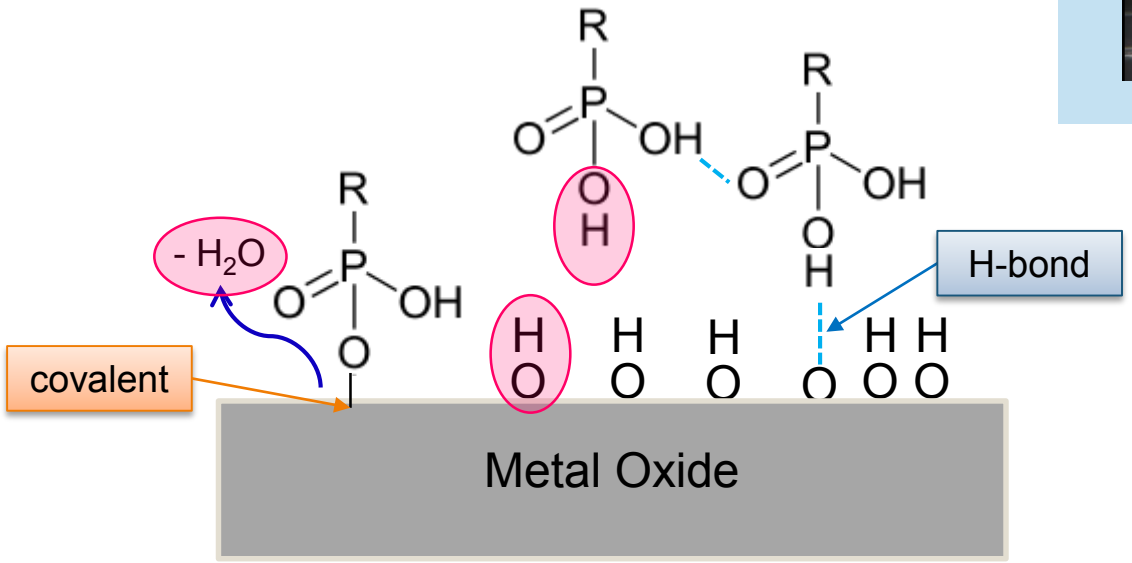
1 min Air then exposed to PA

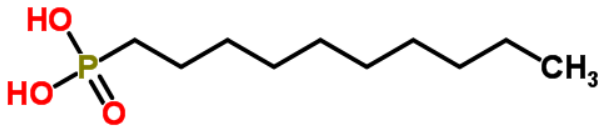


SUMMARY - Protecting the Oxide Layer Prevents Sticking to Channel Inner Walls



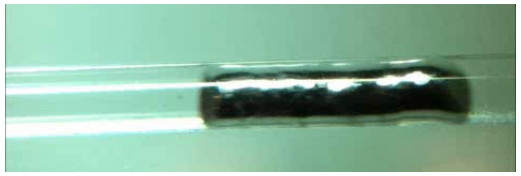
Glass Capillary filled with



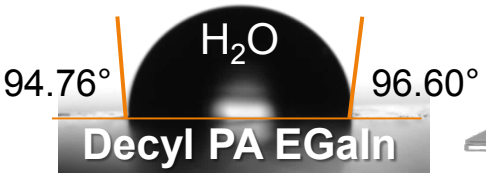


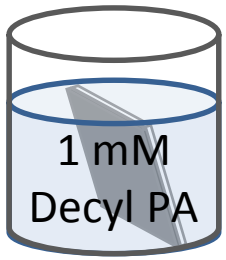
PA: phosphonic Acids

SUMMARY – Decyl Phosphonic Acids Strongly Bind to Ga-Oxide/EGaIn

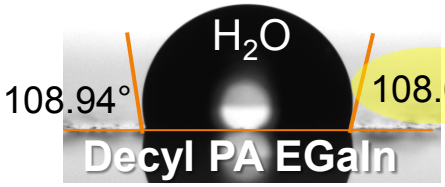


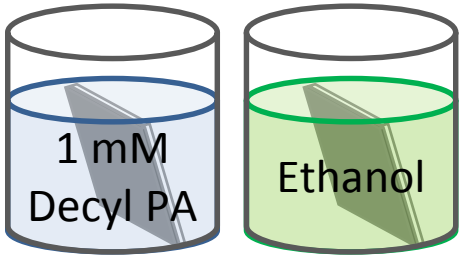
1 mM Decyl PA, 5 min



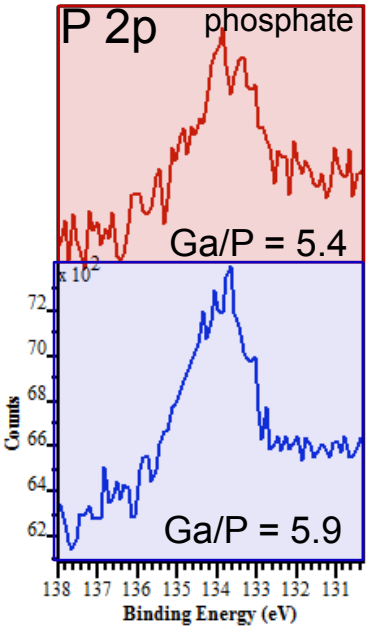


1 mM Decyl PA, 5 min
Ethanol, 17 hours





XPS



Acknowledgment

AFRL Team:

Chris Tabor, Brad Cumby,
Alex Cook, Michael Durstock

Collaborators:

Michael Dickey - North Carolina State Univ.
Jason Heikenfeld - University of Cincinnati